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# ELECTROLYTIC DISSOCIATION

The
Co.

# THE THEORY

OF

# ELECTROLYTIC DISSOCIATION

AND

# SOME OF ITS APPLICATIONS

BY

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# PREFACE

During the last few years the writer has been frequently asked, directly and by letter: Where can an account of the newer developments in physical chemistry be obtained? Where can we learn something about the relation between osmotic pressure and gas pressure, and about the origin and significance of the theory of electrolytic dissociation? The most satisfactory reply which could be made was, read certain original papers. But these were not always accessible, and, in some cases, not quite adapted to the state of development of the reader. While it is true that certain chapters in some of the text-books on physical chemistry are helpful in the direction indicated, yet no one of them seemed to meet entirely the demands of a large number of students.

This little volume has been written with the hope of supplying students of chemistry, physics, and physical chemistry with at least a part of the information which they desire. It aims to give an account of the origin and significance of these newer developments. A student who has a fair knowledge of the origin of the theory of electrolytic dissociation, of the evidence upon which it rests, and of its applications, has already acquired an elementary conception of many of the fundamental principles which underlie modern physical chemistry.

In order that the relation between the newer and the older physical chemistry may be the better understood, a

chapter is devoted to the latter. A few typical pieces of work in the earlier period are considered very briefly, and some of the conclusions reached are pointed out. It is hoped, in this way, to show clearly the nature of the problems solved, the methods employed, and some of the results obtained.

The origin and development of the theory are then taken up. This is followed by an examination of some of the more important lines of evidence bearing upon the theory; and, finally, some applications of the theory in chemistry, physics, and biology are considered.

The attempt is made to answer, in part, the questions: What was physical chemistry before the theory of electrolytic dissociation arose? How did the theory arise? Is it true? What is its scientific use?

It is believed that a closer acquaintance with the facts will but serve to increase the interest in physical chemistry, which is already manifesting itself in so many directions.

I wish to express my indebtedness to my friend Dr. S. H. King, for valuable assistance in reading the proof of this volume.

HARRY C. JONES.

JOHNS HOPKINS UNIVERSITY,
October, 1899.

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# ELECTROLYTIC DISSOCIATION

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# ELECTROLYTIC DISSOCIATION

## CHAPTER I

### THE EARLIER PHYSICAL CHEMISTRY

#### RELATIONS BETWEEN PROPERTIES AND COMPOSITION, AND PROPERTIES AND CONSTITUTION

**Introduction.** — Such marked advances have been made in physical chemistry during the last few years, that it is sometimes thought that this is distinctively a new branch of science. Indeed, the beginning of physical chemistry is often regarded as contemporaneous with the origin of the theory of electrolytic dissociation.

While it is true that the new physical chemistry, which has revolutionized so many of our chemical conceptions, has grown up around the theory of electrolytic dissociation, nevertheless, we must not forget that the newer is built upon, and incorporates, the entire work of the century. Indeed, the theory of electrolytic dissociation itself had its beginning, as we shall see, about the middle of the century.

What was termed physical chemistry, prior to 1885, was largely a study of the physical properties of chemical substances, and work of this kind is in progress up to the present. At first, the physical properties of the ele-

ments, and of compounds, attracted attention, with the result, that the laws of gases, liquids, and solids were discovered. The earlier workers in this field, however, were not content with a disjointed knowledge of the properties of substances; they began to look for, and discover, relations; for the highest aim of scientific investigation is to find out relations between apparently disconnected facts — to discover generalizations. The first point which would naturally be taken up was the relation between properties and chemical composition. How would the introduction of an oxygen or a chlorine atom into a compound affect the physical properties of the compound; or the introduction of a $CH_2$ group into organic compounds alter their properties? The study of this relation was comparatively simple. It was only necessary to prepare a compound, study its properties, then introduce an oxygen or chlorine atom, or a $CH_2$ group, and study the properties of the new compound formed. By applying this process to a large number of substances, relations between composition and properties could be discovered, and much valuable work was done along this line.

But it was well known that there are many chemical compounds which have the same composition, but very different physical properties. Isomeric substances in general have different physical properties. Isomeric substances have the same kind of atoms in the molecule; but there is the possibility that the molecule of one isomeric substance may be the simplest possible, and the molecule of the other isomeric substance may be an aggregate of the simplest molecules; and this might account for the difference in properties of isomeric substances.

There are also other substances, called metameric, which have not only the same kind of atoms in the molecule, but the same number of the same kind of atoms; and yet have different physical properties.

The composition of the molecules in the two cases is exactly the same, so that the difference in properties, in such cases, cannot be attributed to a difference either in the kind or number of atoms in the molecule. To what then is the difference in properties in such cases to be attributed? If it is due neither to the kind, nor to the number of atoms in the molecule, it must be due to the way in which the atoms are combined with one another in the molecule. This brings us to the second problem which was investigated by the earlier physical chemists, the relation between properties and constitution.

In investigating this point, such questions arose as what would be the effect on the physical properties, produced by oxygen in the carbonyl condition (CO), with respect to oxygen in the hydroxyl condition (OH)? Or how would carbon atoms combined as in ethylene $\left(\begin{matrix}C\\ \|\\ C\end{matrix}\right)$ differ in their effect on the physical properties of the compound, from carbon atoms combined as in ethane $\left(\begin{matrix}C\\ |\\ C\end{matrix}\right)$? By using metameric compounds such questions could be, and in a number of cases have been, answered.

Work of this earlier kind had to do with gases, liquids, and solids, but we will confine ourselves to that which has been done upon liquids; since relations have been more fully developed here than for either gases or solids.

**The Boiling-points of Liquids.** — A relation between the boiling-points of liquids and their composition was first pointed out by Kopp,[1] in 1842. An elaborate investigation on the boiling-points of a large number of organic compounds was published in 1858,[2] the result of which was to show that his earlier generalization was, in the main, correct. The following are a few of the data obtained by Kopp, and these will suffice to bring out the relation between composition and boiling-point discovered by him: —

| Substance | | Boiling-point | |
|---|---|---|---|
| Methyl alcohol, | $CH_4O$ | 65° | |
| | | | 13° |
| Ethyl alcohol, | $C_2H_6O$ | 78° | |
| | | | 18° |
| Propyl alcohol, | $C_3H_8O$ | 96° | |
| | | | 13° |
| Butyl alcohol, | $C_4H_{10}O$ | 109° | |
| | | | 23° |
| Amyl alcohol, | $C_5H_{12}O$ | 132° | |
| Ethyl formate, | $C_3H_6O_2$ | 55° | |
| | | | 19° |
| Ethyl acetate, | $C_4H_8O_2$ | 74° | |
| | | | 22° |
| Ethyl propionate, | $C_5H_{10}O_2$ | 96° | |
| Formic acid, | $CH_2O_2$ | 105° | |
| | | | 12° |
| Acetic acid, | $C_2H_4O_2$ | 117° | |
| | | | 25° |
| Propionic acid, | $C_3H_6O_2$ | 142° | |
| | | | 14° |
| Butyric acid, | $C_4H_8O_2$ | 156° | |
| | | | 20° |
| Valeric acid, | $C_5H_{10}O_2$ | 176° | |

[1] Liebig's Ann., 41, 86, 169 (1842).

[2] *Ibid.*, 96, 1 (1858).

Take succeeding members of any of the above three groups of compounds; they differ in composition by one carbon atom and two hydrogen atoms, — by the group $CH_2$, — and there is, in every case, an approximately constant difference between the boiling-points of succeeding members. This relation between composition and boiling-point, Kopp formulated from data obtained much earlier, as follows: *Equal differences in the chemical composition of organic compounds correspond to equal differences in the boiling-points.*

It is obvious from the above data that this relation holds only approximately.

If the above relation held rigidly, then isomeric substances having the same composition must have the same boiling-point. The following data will serve, in part, to show the validity of this conclusion: —

| Substance | Boiling-point |
|---|---|
| Methyl acetate | 56° |
| Ethyl formate | 55° |
| Methyl butyrate | 95° |
| Ethyl propionate | 96° |
| Methyl valerate | 115° |
| Amyl formate | 116° |
| Ethyl butyrate | 115° |

We might conclude from the above data, that isomeric compounds have the same, or very nearly the same, boiling-point. It should be observed, however, that the above isomeric compounds have similar constitution. As soon as isomeric compounds which have different constitution

were compared, it was found that they have very different boiling-points; which shows that boiling-point is conditioned not simply by the number and kind of atoms in the molecule, but also by the way in which these atoms are combined with one another.

Subsequent work has shown that these relations, pointed out by Kopp, are only rough approximations. Dittmar[1] has proved that metameric compounds, such as methyl acetate and ethyl formate, do not have the same boiling-point, and more accurate work on the boiling-points of homologous series of compounds has shown that the difference between the boiling-points of succeeding members is not constant, but usually decreases as the compounds become more complex. This is illustrated by the following data, taken from the work of Schorlemmer:[2]—

| Substance | Boiling-point | |
|---|---|---|
| $C_4H_{10}$ | 1° | |
| | | 37° |
| $C_5H_{12}$ | 38° | |
| | | 32° |
| $C_6H_{14}$ | 70° | |
| | | 29° |
| $C_7H_{16}$ | 99° | |
| | | 25° |
| $C_8H_{18}$ | 125° | |
| $C_2H_5Cl$ | 12.5° | |
| | | 33.9° |
| $C_3H_7Cl$ | 46.4° | |
| | | 31.2° |
| $C_4H_9Cl$ | 77.6° | |
| | | 28.0° |
| $C_5H_{11}Cl$ | 105.6° | |

[1] Liebig's Ann. Suppl., 6, 313 (1868).

[2] Liebig's Ann., 161, 281.

| Substance | Boiling-point | |
|---|---|---|
| $C_2H_5Br$ | 39.0° | |
| | | 32.0° |
| $C_3H_7Br$ | 71.0° | |
| | | 29.4° |
| $C_4H_9Br$ | 100.4° | |
| | | 28.3° |
| $C_5H_{11}Br$ | 128.7° | |

Some interesting facts in connection with the relation between constitution and boiling-point have been discovered. Take the benzene hydrocarbons, and compare those in which one hydrogen has been replaced by a group, with those having two hydrogen atoms replaced; and these, in turn, with those having three hydrogen atoms replaced.

| Compounds with One Hydrogen Atom Replaced | Boiling-point |
|---|---|
| $C_6H_5C_2H_5$ | 134° |
| $C_6H_5C_3H_7$ | 152° |
| $C_6H_5C_4H_9$ | (172° calculated) |
| $C_6H_5C_5H_{11}$ | 193° |

| Compounds with Two Hydrogen Atoms Replaced | Boiling-point |
|---|---|
| $C_6H_4(CH_3)_2$ | 139–140° |
| $C_6H_4\begin{matrix}CH_3\\C_2H_5\end{matrix}$ | 159–160° |
| $C_6H_4\begin{matrix}CH_3\\C_3H_7\end{matrix}$ | 175–178° |
| $C_6H_4(C_2H_5)_2$ | 178–179° |

| Compounds with Three Hydrogen Atoms Replaced | Boiling-point |
|---|---|
| $C_6H_3(CH_3)_3$ | 165–166° |
| $C_6H_3\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}$ | 183–184° |

By comparing these three classes of substances, we see that the second boils higher than the first, and the third higher than the second. Between the first and second there is almost a constant difference of about 6°, and between the second and third the difference is just about 6°, and is nearly constant.

The study of a number of classes of primary and secondary compounds has established the fact, that the same difference in constitution produces approximately the same difference in boiling-point.

**Specific Heat of Liquids.** — The specific heat of a liquid is different at different temperatures. In determining specific heats it is, therefore, necessary to choose some temperature for making the measurements, in order that the results may be comparable.

Reis[1] took the mean specific heats between 20° and the boiling-points of the substances investigated. That specific heats may be comparable, it is necessary to refer them to comparable quantities of substances. Molecular quantities are taken, and the molecular heats are compared, to bring out any relations which might exist. A few results for homologous series of alcohols, acids, and hydrocarbons, will serve to bring out any relation between composition and this property.

| Substance | Molecular Heat | |
|---|---|---|
| Methyl alcohol, $CH_4O$ | 21.0 | |
| | | 9.3 |
| Ethyl alcohol, $C_2H_6O$ | 30.3 | |
| | | 10.2 |
| Propyl alcohol, $C_3H_8O$ | 40.5 | |
| | | 10.4 |
| Butyl alcohol, $C_4H_{10}O$ | 50.9 | |
| | | 9.6 |
| Amyl alcohol, $C_5H_{12}O$ | 60.5 | |

[1] Wied. Ann., 13, 447.

| Substance | | Molecular Heat |
|---|---|---|
| Formic acid, | $CH_2O_2$ | 24.2 |
| | | 7.4 |
| Acetic acid, | $C_2H_4O_2$ | 31.6 |
| | | 2 × 7.9 |
| Butyric acid, | $C_4H_8O_2$ | 47.4 |
| | | 8.6 |
| Isovaleric acid, | $C_5H_{10}O_2$ | 56.0 |
| | | 9.6 |
| Caproic acid, | $C_6H_{12}O_6$ | 65.6 |
| Benzene, | $C_6H_6$ | 33.8 |
| | | 8.0 |
| Toluene, | $C_7H_8$ | 41.8 |
| | | 7.0 |
| Ethyl benzene, | $C_8H_{10}$ | 48.8 |
| | | 8.0 |
| Mesitylene, | $C_9H_{12}$ | 56.8 |

The difference between the molecular heats of any two members of a series is nearly constant. This difference corresponds to a difference in composition of $CH_2$, in each series of compounds; yet its value varies somewhat from one series to another.

The effect of constitution on molecular heat can be seen from the following examples of isomeric substances: —

| Substance | | Molecular Heat |
|---|---|---|
| Propyl aldehyde, | $C_3H_6O$ | 32.6 |
| Acetone, | $C_3H_6O$ | 32.6 |
| Butyric acid, | $C_4H_8O_2$ | 47.4 |
| Isobutyric acid, | $C_4H_8O_2$ | 47.6 |
| Allyl alcohol, | $C_3H_6O$ | 38.1 |
| Propyl aldehyde, | $C_3H_6O$ | 32.6 |

Isomeric compounds, having similar constitution, have very nearly the same molecular heats; but if the constitu-

tions are markedly different, as in the last example, then the molecular heats differ widely from one another. This conclusion has been, in the main, confirmed by the work of de Heen.[1]

Schiff[2] found the further relation between specific heat and composition; that the specific heat is nearly the same for large groups of closely related substances. If we represent the specific heat at $t$ degrees, by $St$, we have the following results:—

| Substance | Specific Heat |
|---|---|
| Methyl benzoate | $St = 0.3630 + 0.00075\,t$ |
| Ethyl benzoate | $St = 0.3740 + 0.00075\,t$ |
| Propyl benzoate | $St = 0.3830 + 0.00075\,t$ |
| Benzene | $St = 0.3834 + 0.001043\,t$ |
| Toluene | $St = 0.3834 + 0.001043\,t$ |
| *M*-Xylene | $St = 0.3834 + 0.001043\,t$ |
| *P*-Xylene | $St = 0.3834 + 0.001043\,t$ |
| Acetic acid | $St = 0.444 + 0.001418\,t$ |
| Propionic acid | $St = 0.444 + 0.001418\,t$ |
| Butyric acid | $St = 0.444 + 0.001418\,t$ |

This relation can be generalized as follows:—

*The specific heat of homologous compounds is represented by the formula $c = a + bt$, in which $b$ always has the same value for the different members, and $a$ often has the same, but sometimes slightly different values for the different members.*

Later work by Schiff[3] confirmed his earlier results.

Considerable work has been done on the specific heats

[1] Essai de phys. comp., Brussels, 1883. [2] Liebig's Ann., 234, 300.
[3] Ztschr. phys. Chem., 1, 376.

of aqueous solutions. That of Marignac[1] is to be especially mentioned. He carried out an elaborate investigation of closely related compounds, as chlorides, bromides, iodides, sulphates, nitrates, acetates, etc., with the object of discovering any relations which might exist. The molecular heats of solutions of a number of substances were found to be the sum of two parts; the one depending upon the acid, the other upon the base — they belong to that class of properties which are known as additive. But a large number of substances did not show this regularity, so that no comprehensive generalization was reached.

**Atomic and Molecular Volumes.** — Here, again, to find relations we must use comparable quantities of substances, and it is most convenient to use molecular quantities. If $g$ is the specific gravity, $\frac{1}{g}$ is the specific volume. If $m$ is the molecular weight, $\frac{m}{g}$ is the molecular volume. A number of relations were pointed out by Kopp.[2]

For closely allied compounds, the same difference in composition corresponds to the same difference in molecular volume. This is seen from the following examples:—

| Substance | Molecular Volume | |
|---|---|---|
| $CH_4O$ | 42.1 | |
| | | 20.1 |
| $C_2H_6O$ | 62.2 | |
| $C_2H_4O$ | 56.5 | |
| | | 20.1 |
| $C_3H_6O$ | 77.5 | |

[1] Ann. Chim. Phys. [5], 8, 410.

[2] Liebig's Ann., 41, 79; 96, 153, 303.

| Substance | Molecular Volume | |
|---|---|---|
| $CH_2O_2$ | 41.4 | |
| | | 22.3 |
| $C_2H_4O_2$ | 63.7 | |
| | | 21.7 |
| $C_3H_6O_2$ | 85.4 | |
| | | 21.7 |
| $C_4H_8O_2$ | 107.1 | |

The following generalization was also reached by Kopp: When two atoms of hydrogen are replaced by one of oxygen, the molecular volume is only slightly changed. Thus: —

| Substance | | Molecular Volume |
|---|---|---|
| Methyl alcohol, | $CH_4O$ | 42.1 |
| Formic acid, | $CH_2O_2$ | 41.4 |
| Ethyl alcohol, | $C_2H_6O$ | 62.2 |
| Acetic acid, | $C_2H_4O_2$ | 63.7 |

The relation between molecular volume and constitution was also worked out. A few results for isomeric substances will serve to bring out the conclusion reached.

| Substance | | Molecular Volume |
|---|---|---|
| Acetic acid, | $C_2H_4O$ | 63.7 |
| Methyl formate, | $C_2H_4O$ | 63.4 |
| Methyl valerate, | $C_6H_{12}O_2$ | 149.2 |
| Ethyl butyrate, | $C_6H_{12}O_2$ | 149.3 |
| Propionic acid, | $C_3H_6O_2$ | 85.4 |
| Ethyl formate, | $C_3H_6O_2$ | 85.3 |

Isomeric liquids have the same molecular volumes.

Kopp found, also, that the atomic volumes were not constants, independent of the nature of the atoms with

which any given atom is combined, but varied somewhat. Thus, oxygen in hydroxyl has a different atomic volume from oxygen in carbonyl. Similarly, carbon and nitrogen in their different forms of combination have different atomic volumes. Yet the molecular volumes are, in general, approximately the sum of the atomic volumes.

The following atomic volumes, —

| | Atomic Volume |
|---|---|
| P | 25.5 |
| As | 26.4 |
| Sb | 32.3 |
| Sn | 40.2 |

show the relation which was pointed out by Kopp, that the atomic volumes of the elements are nearly multiples of a constant, the value of the constant lying between 5.1 and 5.9.

The more recent work of Thorpe[1] has shown that isomeric liquids, at their boiling-points, do not always have exactly the same molecular volume, though the difference is not great. While Schiff found that isomeric liquids, in general, have somewhat different molecular volumes, the differences corresponding to the law, that the higher the boiling-point of the substance the higher its molecular volume.

W. Lossen[2] concluded, from a number of pieces of work carried out by his pupils, that we cannot say, in general, that the molecular volume is additive — that it is the sum of the atomic volumes of its constituents. The molecular volume depends not simply on the kind of

[1] Journ. Chem. Soc., 141, 327 (1880). [2] Liebig's Ann., 254, 42, 1889.

atoms in the molecule, but also on the way in which the atoms are combined in the molecule.

It may, however, be stated, that while the molecular volumes of liquids at the boiling-point, are not exactly the sum of the constant atomic volumes, yet they are approximately so; and molecular volume is approximately an additive property.

**Viscosity.** — Some interesting relations between the viscosity of liquids, and their composition and constitution, have been recently pointed out by Thorpe and Rodger,[1] in their elaborate investigation along this line. Although this work has been done very recently, yet it is typical of the earlier work, and, therefore, belongs in this place.

The viscosities were measured by the time required for a liquid to flow through a capillary tube. To calculate the viscosity coefficient, the formula of Slotte was used, —

$$\eta = \frac{c}{(1 + bt)n},$$

in which $\eta$ is the coefficient of viscosity, in dynes per square centimetre, $c$, $b$, and $n$ are constants, varying with the nature of the liquid. To test the influence of composition and constitution on viscosity, this property of some seventy liquids was determined in absolute measure, at all temperatures from 0° to the boiling-points of the liquids.

To compare viscosity coefficients, we must use comparable temperatures, and we will use first the boiling-points of the liquids. As we ascend a homologous series of com-

[1] Thorpe and Rodger, Proceed. Royal Soc., 1894; Bakerian Lecture, Royal Soc. Chem. News, 69, 123, 135; Journ. Chem. Soc., 71, 360; Ztschr. phys. Chem., 14, 361.

pounds, the coefficient generally decreases; in a few cases it remains the same, and in one series increases. If we compare corresponding compounds, we find that the one with the highest molecular weight has the highest coefficient. The effect of increase in molecular weight, however, may be more than counterbalanced by constitution. Iso-compounds have, in general, a larger coefficient than normal compounds. The degree of symmetry of the molecule can have a marked influence on the size of the coefficient.

The following relations between the molecular viscosities at the boiling-point, were established by Thorpe and Rodger. An increment of $CH_2$ in compounds, with the exception of the alcohols, dibromides, and lowest members of the homologous series, corresponds to an increase in the molecular viscosity. The compound having the highest molecular weight, with the exception of the compounds mentioned above, has the highest molecular viscosity. The differences in the molecular viscosities, between corresponding members of two correlated series, are fairly constant.

An attempt was made to calculate the viscosity constants of a number of atoms and groups, but since constitution comes so largely into play, it is evident that these constants are only approximations. Yet, the molecular viscosity of forty-five liquids, calculated from these constants, differs in few cases more than 5 per cent from those found. There are, however, many exceptions to this rule.

The above relations were all obtained by comparing the viscosities of liquids at their boiling-points. But another method of comparison was also used.

The general shape of the viscosity curves, toward the boiling-point, was practically the same. If tangents are drawn to the curves at points corresponding to the boiling-points of liquids, the inclinations of the tangents to the axis, *i.e.* the *slopes* of the curves, varied but little. Curves for the alcohols, etc., were an exception.

The temperatures of equal slope of curves were then taken for comparison. At this point, the effect of temperature would be the same for different substances.

It was found that at the temperature of equal slope, there were more definite relations between the viscosity coefficients and the chemical nature of the compounds. At this temperature a $CH_2$ group exerts a positive influence on the coefficient, which decreases as the series ascends. Exceptions are the alcohols, acids, and dichlorides. Of corresponding compounds, that with the highest molecular weight has the highest coefficient. Iso-compounds invariably have a larger coefficient than normal compounds; while for other isomeric substances a branching of the atomic chain has an influence on the magnitude of the coefficient.

The molecular viscosity at constant slope can be calculated from the fundamental constants for the constituents, but here, again, water and the alcohols are exceptions.

It is evident from the above, that the relations found, thus far, between viscosity and composition and constitution, are, at best, only approximately correct, and apply only to a limited number of cases.

**Refraction of Light.** — A number of attempts have been made to formulate a relation between the power of substances to refract light and their densities. Of these, that

proposed by Dale and Gladstone[1] is probably the most general. If we represent the index of refraction by $n$, and the density by $d$,

$$\frac{n-1}{d} = \text{constant.}$$

They showed that this relation holds for a large number of liquids, within very wide ranges of temperature.

Landolt[2] tested this relation very accurately, for a small range of temperature, and found almost exactly a constant for a number of substances. Others[3] have, however, obtained results to which the above expression did not accurately apply, the value $\frac{n-1}{d}$ either increasing or decreasing with the temperature.

The formula of Dale and Gladstone is far more accurate than the expression $\frac{n^2-1}{d}$, which was proposed earlier, and it is preferable to that of Lorenz-Lorentz,[4] which is: —

$$\frac{1}{d} \cdot \frac{n^2-1}{n^2+2}.$$

Recently, Edwards[5] has tested the formula —

$$\frac{n-1}{nd},$$

and has shown that it holds for a number of substances, over a considerable range of temperature.

None of these expressions, however, are perfectly general, and without the introduction of specific constants, they do not show an exact relation between refractivity

[1] Phil. Trans. (1858), 887. *Ibid.*, 1863.
[2] Pogg. Ann., 123, 595.
[3] *Ibid.*, 132, 202; 133, 1.
[4] Wied. Ann., 11, 70; 9, 641.
[5] Amer. Chem. Journ., 16, 625; 17, 473.

and density. Indeed, it is not at all certain that such a relation exists.

Relations between refractivity, and composition and constitution, have, however, been worked out, and a few of these will now be considered.

Dale and Gladstone[1] found that isomeres of similar constitution have very nearly the same specific refractivity. In homologous series this quantity increases regularly. They drew the general conclusion, that "every liquid has a specific refractivity, composed of the specific refractivities of the elements in the compound, modified by the kind of union."

Landolt[2] compared the "refraction equivalents" of substances, calculating them from the formula —

$$\frac{m(n-1)}{d},$$

in which $m$ is the molecular weight of the substance, and the other symbols have the same significance as in the Dale-Gladstone expression.

The relation between composition and refraction equivalents was worked out, and it was found that equal differences in composition correspond to equal differences in refraction equivalents.

Landolt showed, also, that the refraction equivalent of a compound is approximately the sum of the refraction equivalents of its parts.

He investigated, further, the relation between constitution and refraction equivalents, by studying metameric substances. A few results are given: —

[1] Phil. Trans., 1863. [2] Pogg. Ann., 117, 353; 122, 545; 123, 595.

| Substance | | Refraction Equivalent |
|---|---|---|
| Propionic acid, | $C_3H_6O_2$ | 28.57 |
| Methyl acetate, | $C_3H_6O_2$ | 29.36 |
| Ethyl formate, | $C_3H_6O_2$ | 29.18 |
| Valeric acid, | $C_5H_{10}O_2$ | 44.05 |
| Methyl butyrate, | $C_5H_{10}O_2$ | 43.97 |
| Butyl alcohol, | $C_4H_{10}O$ | 36.11 |
| Ethyl ether, | $C_4H_{10}O$ | 36.26 |

Isomeric substances are thus seen to have the same refraction equivalents.

J. W. Brühl has carried out elaborate investigations, since the year 1880,[1] on the refractive power of liquids. His work, which has now extended over nearly twenty years, has brought to light many interesting and important relations. He took up the effect of carbon, in its different forms of combination, upon refractive power, and showed that doubly united carbon exerted a different influence from carbon united by single bonds. Each double union in a compound increases the refraction equivalent about two units. He thus showed the influence of constitution on refractivity. He also found that oxygen, in its different forms of combination, had different effects on refractivity.

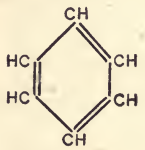
The question of the effect of symmetry on refractive power has also been studied. Two isomeric compounds, the one symmetrical, the other asymmetrical, have been studied with the following results: —

| Substance | Refraction Equivalent |
|---|---|
| Ethylene chloride | 20.95 |
| Ethylidene chloride | 21.08 |
| Ethylene bromide | 26.84 |
| Ethylidene bromide | 27.31 |

[1] Liebig's Ann., 200, 139.

The unsymmetrical compound has a larger refraction equivalent than the symmetrical.

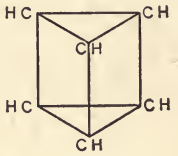
The refraction values of a number of elements have been worked out, and also the differences in the refraction values of certain elements in different forms of combination. Refractivity, therefore, can be and has been used to throw light on the question of constitution. Brühl has applied the method of refractivity to the problem of the constitution of benzene. How are the carbon atoms united in benzene? If by a single bond, they will have a different refractive power than if they were doubly united. From the power of benzene to refract, Brühl was led to the conclusion that there are three single and three double bonds in the molecule, which is expressed thus:—




This is the well-known benzene formula of Kekulé.

It should be stated, that it is not safe to place unlimited confidence in a method like the above for determining the constitution of chemical compounds. The same problem has been attacked by Julius Thomsen, with very different result, using a thermochemical method. Thomsen's method is based upon the principle, that when a compound is burned a different amount of heat is liberated if the carbon atoms are united by single or double bonds, than if they are united by triple bonds. He determined the heat of combustion of benzene, and found that it cor-

responds to nine single bonds between the carbon atoms,[1] which would be expressed thus: —




This is the well-known prism formula of benzene, suggested and defended by Ladenburg. This apparent digression is made, to show the caution which is necessary in accepting conclusions based upon work such as that above described.

**Rotation of the Plane of Polarization.** — When a beam of polarized light is passed through certain liquids, the plane of polarization is changed. Sometimes it is turned in the one direction, sometimes in the other. This property is not confined to liquids, but is possessed also by solids and gases. Substances which have this property are said to be optically active. According as the substance rotates the plane of polarization in the one or in the other direction, it is termed dextro- or lævo-rotatory.

The direction and amount of rotation depend chiefly upon the nature of the substance. The rotation depends, also, upon the thickness of the layer, the wave-length of light, and the temperature. Comparable results can, therefore, be obtained only by keeping all of the conditions constant, and then studying the kind and amount of rotation which different compounds produce.

[1] Ber. d. chem. Gesell., 13, 1808.

The specific rotatory power of a liquid has been defined by Biot, as the rotation produced by a layer one decimetre in length. But since different liquids have different densities, this would contain different amounts of substance. The specific rotatory power $r$ is obtained by dividing the angle $a$, through which a column of liquid of length $l$, and density $d$, rotates the plane of polarization, by $ld$.

$$r = \frac{a}{ld}$$

In order to compare the rotatory power of liquids we must deal with comparable quantities, and most conveniently with molecular quantities. If $m$ is the molecular weight of the substance, this must be multiplied into the above expression. The molecular rotatory power $mr$ would then be : —

$$mr = \frac{ma}{ld}$$

This unit is usually divided by one hundred.

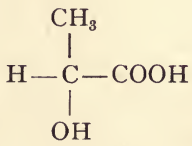
Some exceedingly interesting relations between rotatory power, and composition and constitution, have been worked out. There is quite a large number of substances which exist in different forms, one rotating the plane of polarization to the right, the other to the left. Pasteur[1] pointed this out in connection with the tartaric acids. There is a dextro-rotatory tartaric acid, and a lævo-rotatory tartaric acid, and inactive racemic acid. The latter is produced by mixing solutions of the dextro- and lævo-varieties, and, on the other hand, racemic acid can be separated into dextro- and lævo-tartaric acids. This separation is accomplished

[1] Ann. Chim. Phys., 28, 56 (1850).

by preparing the sodium-ammonium salt of racemic acid, and allowing it to crystallize. Salts of dextro- and lævo-tartaric acids will separate, and can be distinguished by the difference in crystal forms. Certain right-handed hemihedral planes appear on the salt of the dextro-acid, and left-handed planes on the salt of the lævo-acid. There is also a fourth tartaric acid, which is inactive, but this can be transformed into the other modifications.

There are several other examples known of a substance existing in a dextro- and lævo-modification, and also in an inactive form; and by combining the active modifications, the inactive is formed, and from the inactive form the active may be obtained.

A direct study of the relation between optical activity, and composition and constitution, will be considered more in detail. We will deal with the compounds of carbon. It was observed by the French chemist, Le Bel,[1] and a little later by van't Hoff,[2] that every carbon compound which is optically active can be represented as containing a carbon atom in combination with four different atoms or groups. Take the simplest case, that of lactic acid. We have :—



Le Bel ascribed optical activity to the asymmetrical nature of such an arrangement, but van't Hoff went much far-

[1] Bull. Soc. Chim. [2], 22, 337 (1874).
[2] *Ibid.*, 23, 295 (1875).

ther, and tried to show how the atoms are actually arranged in space. He represented the central carbon atom of the system, as placed at the centre of a regular tetrahedron, with its four bonds acting in the directions of the solid angles. At those angles are placed the four atoms, or groups, in combination with the central carbon atom. If these atoms, or groups, are the same, we would have a perfectly symmetrical arrangement, and every atom would bear the same relation to the molecule as every other atom. Take the case of marsh gas, the four hydrogen atoms should each bear the same relation to the molecule, and such has been shown to be the case by the elaborate work of Henry. If either two of the atoms, or groups, at the corners of the tetrahedron are the same, then it is impossible to so arrange them that two tetrahedra, containing the same four groups at the corners, could not be completely superimposed. But if all four atoms, or groups, are different, then two tetrahedra containing these at the corners can never be superimposed, but bear the relation to one another of an object and its image in a mirror.

If this asymmetrical arrangement is the cause of optical activity, then only those carbon compounds could be optically active which have four different atoms, or groups, combined with the central carbon atom. Of all the cases of optical activity known among carbon compounds, there is only one possible exception. Baeyer[1] has described a dipentene, which he thinks does not contain an asymmetric carbon atom, and which is, however, optically active. But this cannot be cited as a positive exception, since the constitution of this substance is not definitely established.

[1] Ber. d. chem. Gesell., 27, 454.

Another consequence of the van't Hoff theory is, that whenever a dextro-rotatory substance appears, a lævo must also be formed, and such is the fact. Of the large number of cases known, there is no exception to this rule.

If optical activity is due to the presence of an asymmetric carbon atom, then, whenever we have such a carbon atom present, we ought to have optical activity. There are, however, many compounds known, which contain an asymmetric carbon atom, yet do not show optical activity. This is explained by assuming that there are present an equal number of dextro- and lævo-molecules, and optical inactivity is the result. Similarly, if there are two asymmetric carbon atoms in the same molecule, these may exactly neutralize each other's influence on polarized light, as in the case of the fourth variety of tartaric acid.

It is difficult to overestimate the importance of these suggestions by Le Bel and van't Hoff. They underlie all that has been done along the line of stereochemistry, and this is certainly one of the most important advances which has been made in organic chemistry in the last quarter of a century.

This suggestion of the tetrahedron as the spatial arrangement in carbon compounds has been developed much farther by Wislicenus[1] than was done by van't Hoff. The former has shown how this arrangement is capable of accounting satisfactorily for the transformations of maleïc and fumaric acids; of the malic acids; and, what is even more interesting, it furnishes a beautiful explanation of

[1] Monograph, Ueber die räumliche Anordnung der Atome in organischen Molekülen, Leipzig.

the optical behavior of the four tartaric acids; facts which hitherto had been empirically established, but whose significance was entirely unknown. While space will not permit us to enter into a discussion of this monograph by Wislicenus, yet we should again call attention to its unusual interest and importance for all who are interested in the philosophy of organic chemistry.

The suggestion by van't Hoff to account for optical activity has been further extended by Guye.[1] If optical activity is due to the groups being different at the four corners of the tetrahedron, — to an asymmetrical arrangement, — then by changing the degree of asymmetry, the degree of optical activity ought also to be changed. If we have a carbon atom surrounded by four different atoms or groups, the centre of gravity of the system will lie off of the planes of symmetry. If now we replace one of the atoms or groups by one having a greater weight, the centre of gravity of the system will be moved toward the heavier substituent. By changing the masses of the atoms or groups, the centre of gravity of the system can be changed, first in one and then in another direction.

Guye has shown, in a large number of cases, that as the centre of gravity of the system is changed, by introducing lighter or heavier groups, the optical activity of the substance changes, and in the way that would be expected. As the asymmetry was increased, optical activity in general increased.

By introducing groups of the weights desired, the centre of gravity could often be changed from one side of the molecule to the other, and in a number of such cases the

[1] Compt. rend., 110, 714.

nature of the rotation was changed — a dextro-rotatory substance becoming lævo-rotatory, and the reverse.

There are some cases known which cannot be entirely reconciled with the views of Guye. Work of this kind is undoubtedly of the very highest importance, since it throws light on the inner arrangement of the atoms and groups in the molecule.

Another outcome of the stereochemical conception of van't Hoff, with respect to carbon, is the recent work which has been done on the stereochemistry of nitrogen. Hantzsch and Werner[1] have shown, that if we represent the nitrogen atom as being placed at one of the angles of a tetrahedron, we can explain the differences in constitution which undoubtedly exist between many of the isomeric substances containing nitrogen; differences for which it is impossible to account, in many cases, by the ordinary methods of representing constitution, which do not take into account spatial relations.

Although the work of Wislicenus, Guye, and Hantzsch and Werner was done in the last few years, yet it is the direct outcome of the suggestion made by van't Hoff in 1875, which is more than ten years before the newer developments in physical chemistry began. It, therefore, seems not to be entirely out of place to refer to this recent work under the head of the earlier physical chemistry, of which it is the direct consequence.

**Magnetic Rotation of the Plane of Polarization.** — It was discovered by Faraday,[2] that substances in general have the power to rotate the plane of polarization of light, when placed in a suitable position in a magnetic field. An electro-

[1] Ber. d. chem. Gesell., 23, 11, 1243, 2764, 2769. [2] Pogg. Ann., 68, 105.

magnetic field is the most convenient, the current flowing in a plane at right angles to the direction in which the ray of light moves. The amount of rotation depends on the strength of the magnetic field, length of layer of substance, the temperature, and the nature of the substance. To discover any relations between magnetic rotation and composition, every one of the above conditions must be kept constant, from one substance to another.

The work of Becquerel[1] brought out some relations, such as that the rotatory power of the alcohols increased with increase in molecular weight; but by far the most elaborate investigation of this phenomenon we owe to W. H. Perkin.[2] He chose as his unit the molecular rotation of water, and compared other substances with it. A few examples are given: —

| Substance | Molecular Rotation | |
|---|---|---|
| Methyl alcohol, $CH_4O$ | 1.640 | |
| | | 1.14 |
| Ethyl alcohol, $C_2H_6O$ | 2.780 | |
| | | 0.988 |
| Propyl alcohol, $C_3H_8O$ | 3.768 | |
| Formic acid, $H_2CO_2$ | 1.617 | |
| | | 0.908 |
| Acetic acid, $C_2H_4O_2$ | 2.525 | |
| | | 0.937 |
| Propionic acid, $C_3H_6O_2$ | 3.462 | |
| | | 1.010 |
| Butyric acid, $C_4H_8O_2$ | 4.472 | |

These results, taken from a large number, show, for a homologous series, a constant difference in the magnetic

[1] Ann. Chim. Phys. [4], 22, 5. [2] Journ. prakt. Chem. [2], 31, 481; 32, 523.

rotation produced by the constant difference in composition of $CH_2$. The effect of constitution on magnetic rotation can be seen by comparing isomeric compounds.

| Substance | | Magnetic Rotation |
|---|---|---|
| Propyl alcohol, | $C_3H_8O$ | 3.768 |
| Isopropyl alcohol, | $C_3H_8O$ | 4.019 |
| Ethylene chloride, | $C_2H_4Cl_2$ | 5.485 |
| Ethylidene chloride, | $C_2H_4Cl_2$ | 5.335 |

These examples suffice to bring out the fact, that isomeric substances have different magnetic rotation, showing the effect of constitution on this property.

Perkin has continued his work on magnetic rotation up to the present, and some of his more important communications are referred to below.[1]

J. W. Rodger and W. Watson[2] have published an investigation on magnetic rotation, where a stronger magnetic field was used, and, consequently, the amount of rotation to be measured was greater. Their paper is devoted mainly to a description of their apparatus, and contains too few results to warrant any generalization. It is to be hoped that this work will be continued, using the stronger magnetic field.

**Conclusion from the Preceding Work.** — On examining the work thus far described, we are impressed by the large number of relations which have been pointed out between physical properties, and composition and constitution. But we are also impressed by the fact that these relations

[1] Chem. News, 60, 253; 62, 255; 64, 19; 65, 284; 66, 277; 67, 143; 68, 302; 69, 224; 71, 123; 73, 301. Journ. Chem. Soc., 59, 981; 61, 287; 61, 800; 65, 815; 69, 1025. Ztschr. phys. Chem., 21, 451; 21, 671.

[2] Ztschr. phys. Chem., 19, 323.

are only approximations; they are not sharply defined and rigorous. A relation was often discovered, which, at first, seemed to be fairly exact, but as the experimental work became more refined, a larger number of exceptions appeared. Thus, in many cases, what seemed to be a quantitative relation was merely a qualitative one.

We feel, throughout this entire work, the purely empirical nature of the generalizations reached, and that they are very incomplete expressions of the truth. There is a lack of any definite, mathematical conception, in terms of which this earlier work can be interpreted.

**The Study of Solutions.** — The physical properties of substances may be studied when they are isolated, or when they are mixed with other substances. Under the latter condition, one substance is said to be dissolved in the other, and we have to do with solutions. A number of the properties of solutions were early investigated. Graham[1] studied the phenomenon of diffusion, and Fick[2] pointed out that diffusion depends upon, and is proportional to, the difference in concentration of the solutions. Blagden[3] discovered, more than a hundred years ago, that the lowering of the freezing-point of water by a dissolved substance is proportional to the amount of substance present. The same fact was rediscovered by Rüdorff,[4] and, later, Coppet[5] showed that the molecular lowering of the freezing-point, produced by closely allied substances, is very nearly constant.

Raoult[6] studied the freezing-point lowering of solutions

[1] Liebig's Ann., 77, 56, 129; 80, 197.
[2] Pogg. Ann., 94, 59.
[3] Phil. Trans., 78, 277.
[4] Pogg. Ann., 114, 63; 116, 55; 145, 599.
[5] Ann. Chim. Phys. [4], 23, 366; 25, 502; 26, 98.
[6] Compt. rend., 94, 1517; 95, 188, 1030; Ann. Chim. Phys. [6], 2, 66.

in solvents other than water, and arrived at the generalization, that a molecule of any substance, in one hundred molecules of a solvent, lowers the freezing-point of the solvent by a nearly constant amount. These investigations by Raoult on freezing-point lowering were very elaborate, including a large number of solutions in acetic acid, formic acid, benzene, nitrobenzene, ethylene bromide, etc.

The lowering of the vapor-pressure of a solvent by a dissolved substance was early investigated. Wüllner[1] pointed out that the lowering of the vapor-pressure of water by dissolved substances is proportional to the amount of substance, and Raoult[2] studied the influence of temperature, concentration, and nature of dissolved substance, on the depression of the vapor-tension of the solvent. Raoult[3] worked with a number of solvents, and found that the depression of the vapor-tension produced by one molecule of substance in one hundred molecules of solvent was the same for different solvents. Raoult also showed how the lowering of the freezing-point of a solvent by a dissolved substance, and also the lowering of its vapor-tension, may be used to calculate the molecular weight of the substance in solution.

**Other Lines of Work.** — The earlier physical chemists were not all engaged with problems such as we have been considering. They measured the heat liberated in chemical reactions. They studied the behavior of substances when submitted to the action of the electric current. The velocity with which chemical reactions take place, and the conditions of equilibrium, were investigated. And the dif-

[1] Pogg. Ann., 103, 529; 105, 85; 110, 564. [2] Compt. rend., 103, 1125.
[3] *Ibid.*, 104, 1430; Ann. Chim. Phys. [6], 15, 375; Ztschr. phys. Chem., 2, 353.

ferent powers of substances to react, as depending upon their composition and constitution, were carefully determined.

This brief account of the nature and condition of physical chemistry, before the theory of electrolytic dissociation arose, would be unsatisfactory, and, perhaps, misleading, without some statement as to the development of thermochemistry, electrochemistry, and chemical affinity. By knowing the condition of the several branches of physical chemistry, before the new conceptions arose, we can see the more clearly what changes have been introduced, what advances made by them.

### THE DEVELOPMENT OF THERMOCHEMISTRY

The quantitative study of the amount of heat liberated in chemical reactions was begun very early, and has been continued from the time of Robert Boyle to the present. The problem, in one form or another, has attracted the attention of men like Davy, Lavoisier, and Laplace. Indeed, the very important discovery was made by the last two,[1] that just as much heat is required to decompose a compound into its constituents as was liberated when the constituents united to form the compound. But the beginning of modern thermochemistry dates from the time of G. H. Hess.[2]

**Work of Hess.** — Hess discovered the principle which has come to be known as the "Constancy of the sum of the heats of reaction." If a chemical transformation takes place in one stage, a certain amount of heat is liberated, which we will call *a*. If the transformation takes place in

[1] Œuv. de Lav., II, 287. [2] Pogg. Ann., 50, 385 (1840).

two stages, in which, respectively, $h$ and $c$ amounts of heat are liberated, we always have, $h + c = a$. This is perfectly general, regardless of the number of stages involved in the transformation. The discovery of this principle makes it possible to study, thermochemically, a great number of reactions which are comparatively complex taking place in more than one stage.

In addition to this important discovery, Hess made another of very wide significance. He observed that when solutions of neutral salts are mixed, there is little or no heat liberated or absorbed. He concluded, that the heat consumed in decomposing the salts was exactly equal to that liberated in the formation of the new salts with acid and base interchanged, since it was known that under the conditions that solutions of two salts are mixed, four salts are always formed, provided all four are easily soluble and no precipitate is produced. This has come to be known as Hess's law of the thermoneutrality of salts. The significance of this law was not understood until it was fully explained by the theory of electrolytic dissociation.

**Favre and Silbermann.** — We now come to the beautiful thermochemical investigations of Favre and Silbermann.[1] They greatly improved the apparatus and method used in thermochemical measurements. The calorimeter which they devised is the same in principle as every form used since their time. They carried out elaborate thermochemical investigations, which were undoubtedly the most accurate up to their time.

Thermochemical investigations since the time of Favre

[1] Ann. Chim. Phys. [3], 34, 357; 36, 1; 37, 406.



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and Silbermann have centred around two men: Berthelot in Paris, and Julius Thomsen in Copenhagen. Much work has also been done by pupils of these men, either working with them or independently.

**Work of Berthelot.** — Berthelot[1] began his very elaborate thermochemical investigations in 1865, and these have extended over a long period. The results of his work are published in his well-known book, of two volumes, "Essai de Mécanique Chimique." The three principles which he developed in his work are: —

First, the heat liberated in a chemical reaction depends only on the condition of the system at the beginning and at the end, and not at all on the intermediate stages.

Second, the heat evolved in a chemical process is a measure of the corresponding chemical and physical work.

Third, every chemical reaction tends to form those substances which are formed with the greatest evolution of heat.

This last principle has come to be known as the law of maximum work, but would better be known as the law of maximum heat evolution.

The last of the three principles announced by Berthelot has attracted by far the most attention. As an expression of a perfectly general truth, it is, of course, not exact. There are many exceptions known to it, and some of these were recognized and pointed out by Berthelot himself. And yet, notwithstanding the exceptions, if one will carefully read the "Essai de Mécanique Chimique," the impression is almost sure to be left that here is, at least, the kernel of a great truth, even if it is expressed in an imperfect and not sufficiently comprehensive manner.

[1] Ann. Chim. Phys. [4], 6, 290; 28, 94.

Much of the criticism of this third principle, whether its true discoverer be Berthelot[1] or Julius Thomsen,[2] is evidently not entirely well founded, if all that Berthelot has written concerning it is taken into account.

**Work of Julius Thomsen.** — The thermochemical work of Julius Thomsen has been collected into four volumes, and published under the title of "Thermochemische Untersuchungen." This, taken as a whole, undoubtedly contains the most elaborate and accurate thermochemical measurements which have ever been made.

In order that a reaction may be studied thermochemically, one condition is that it should proceed rapidly to the end. Many reactions between organic compounds do not fulfil this condition. Indeed, most organic reactions are relatively slow. To study such reactions thermochemically, some means must be devised which would accelerate the velocity of the reaction. Berthelot[3] improved the form of apparatus which had already been suggested for this purpose. A thick-walled, steel cylinder, lined on the inside with platinum or enamel, is used for accelerating the velocity of such reactions as organic combustions. The substance to be burned is placed on a suitable arrangement, and introduced into the "bomb." This is then tightly closed, and filled with oxygen under high pressure. The substance is ignited by an electric current; the combustion proceeds very rapidly, and the heat set free is measured in some convenient form of calorimeter. The use of the Berthelot bomb has greatly widened the field of thermochemical investigation.

[1] Ann. Chim. Phys. [5], 4, 6; [4], 18, 103. [2] Ber. d. chem. Gesell., 6, 423.
[3] Ann. Chim. Phys. [5], 23, 160.

Some of the most accurate thermochemical measurements, in which the bomb has been employed, have been made by Stohmann,[1] in Leipzig (who worked for a time with Berthelot), and by his assistant, Langbein.

**Thermochemical Results.** — A few thermochemical results will suffice to bring out the kind of relations which have been discovered by such work.

The heat evolved when acids and bases neutralize each other has been carefully investigated. We will give a few results for the strong acids and strong bases: —

$$NaOH + HNO_3 = 13680 \text{ cal.}$$
$$NaOH + HClO_3 = 13760 \text{ cal.}$$
$$NaOH + HBrO_3 = 13780 \text{ cal.}$$
$$NaOH + HIO_3 = 13810 \text{ cal.}$$
$$NaOH + HCl = 13700 \text{ cal.}$$
$$NaOH + HBr = 13700 \text{ cal.}$$
$$NaOH + HI = 13700 \text{ cal.}$$

In the above table the base is kept constant and the acid changed; yet the heat of neutralization of equivalent quantities is nearly a constant. A few results will be cited in which a given acid is neutralized with a number of bases: —

$$KOH + HCl = 13700 \text{ cal.}$$
$$\tfrac{1}{2}Ba(OH)_2 + HCl = 13900 \text{ cal.}$$
$$\tfrac{1}{2}Sr(OH)_2 + HCl = 13800 \text{ cal.}$$
$$\tfrac{1}{2}Ca(OH)_2 + HCl = 13900 \text{ cal.}$$

Here, again, the heat of neutralization is nearly a constant, and the same constant as in the preceding case. It can, therefore, be stated, that the heat liberated, when-

[1] Journ. prakt. Chem., 33, 241; 35, 40; 39, 509; 40, 341; 42, 367; 43, 1; 44, 336; 45, 332.

ever a strong acid is neutralized by a strong base, is a constant, within experimental error, independent of the nature of the acid and of the base. If either the acid or base is weak, a different heat of neutralization is found.

The meaning of these facts was entirely unknown at the time of their discovery. Why should the heats of neutralization of strong acids and strong bases be a constant, and why should the heats of neutralization of weak acids and bases be different? These were questions whose meaning was not even suspected before the theory of electrolytic dissociation was proposed. These facts, as we shall see, are not only explicable in terms of that theory, but are a necessary consequence of it. Indeed, the constancy of the heat of neutralization of strong acids and strong bases is a very good argument in favor of the correctness of the new theory, and this argument is even strengthened by the fact that weak acids and bases have a different heat of neutralization.

Certain relations between the composition and constitution of organic compounds and their heats of combustion have been worked out. Take the marsh-gas series of hydrocarbons.

| Substance | Heat of Combustion | |
|---|---|---|
| Methane, $CH_4$ | 211900 cal. | |
| | | 158500 cal. |
| Ethane, $C_2H_6$ | 370400 cal. | |
| | | 158800 cal. |
| Propane, $C_3H_8$ | 529200 cal. | |
| | | 158000 cal. |
| Butane, $C_4H_{10}$ | 687200 cal. | |
| | | 159900 cal. |
| Pentane, $C_5H_{12}$ | 847100 cal. | |

A difference of $CH_2$ produces very nearly a constant difference in the heats of combustion of these hydrocarbons. The constitution of these compounds seems to have no effect.

The following results were obtained for the ethylene hydrocarbons: —

| Substance | | Heat of Combustion | |
|---|---|---|---|
| Ethylene, | $C_2H_4$ | 333400 cal. | |
| | | | 159300 cal. |
| Propylene, | $C_3H_6$ | 492700 cal. | |
| | | | 157900 cal. |
| Isobutylene, | $C_4H_8$ | 650600 cal. | |
| | | | 157000 cal. |
| Amylene, | $C_5H_{10}$ | 807600 cal. | |

A constant difference in the heats of combustion is observed here, also, for the constant difference in composition of $CH_2$; and this is the same difference as in the case of saturated hydrocarbons. The heats of combustion of the two series are not the same, because, in addition to two hydrogen atoms more in one system than in the other, we have doubly united carbon atoms. And whenever there is double or triple union between the carbon atoms, the heat of combustion is affected by it.

The halogen substitution products of the marsh-gas hydrocarbons show, also, constant differences in the heats of formation: —

| | | | Dif. | | | Dif. |
|---|---|---|---|---|---|---|
| $CH_3Cl$ | 22000 cal. | $CH_3Br$ 14200 cal. | 7800 cal. | $CH_3I$ | 2800 cal. | 19200 cal. |
| $C_2H_5Cl$ | 29600 cal. | $C_2H_5Br$ 21800 cal. | 7800 cal. | $C_2H_5I$ | 9900 cal. | 19700 cal. |
| $C_3H_7Cl$ | 36000 cal. | $C_3H_7Br$ 29100 cal. | 6900 cal. | | | |

Relations appear for the alcohols which are similar to those found for the hydrocarbons. The difference

between the heats of combustion of members of a homologous series of alcohols is nearly constant, as the following results will show: —

| Substance | Heat of Combustion | |
|---|---|---|
| Methyl alcohol, $CH_4O$ | 182200 cal. | |
| | | 158300 cal. |
| Ethyl alcohol, $C_2H_6O$ | 340500 cal. | |
| | | 158100 cal. |
| Propyl alcohol, $C_3H_8O$ | 498600 cal. | |

The effect of constitution on heat of combustion is seen in the fact, that primary alcohols have larger heats of combustion than either secondary or tertiary. An interesting application of the effect of constitution on heat of combustion has been made by Julius Thomsen, in the case of benzene, to which reference has already been made.

## THE DEVELOPMENT OF ELECTROCHEMISTRY

The decomposition of chemical compounds by the electric current has attracted the attention of physicists and chemists ever since the discovery of the voltaic element at the close of the last century. The comparatively insignificant elements which were first constructed sufficed, however, to effect a number of decompositions, such as the electrolysis of metal salts, of water to which acid has been added, etc. But it remained for Sir Humphry Davy[1] to construct the large voltaic element which effected such remarkable decompositions, and led to the discovery of the alkali metals. The current from his element was passed through the fused oxides of potassium and sodium, when small globules were seen to rise to the surface of the mol-

[1] Gilb. Ann., 7, 114 (1801).

ten mass, and take fire on contact with the air. Thus were sodium and potassium first separated from their compounds.

**Davy's Electrochemical Theory.** — The direct decomposition of the oxides of the alkali metals by the electric current, also the decomposition of acidulated water, and a large number of other chemical substances, pointed to some close relation between chemical attraction and electrical attraction. As the net result of his very elaborate electrochemical studies, Davy was led to the electrochemical theory which bears his name. The atoms of substances, by contact, acquire different electrical charges, and these atoms then attract one another, because they are charged, the one positive, and the other negative. These charges may be so slight, that the attraction between them will not be sufficient to cause the atoms to change their former relations, or they may be great enough to effect such a rearrangement, when a chemical compound will be formed. Chemical attraction between atoms is, then, but the electrical attraction between the opposite charges which have accumulated upon them, due to their contact with one another.

Electrolysis consists in destroying the difference between the charges upon the atoms in the compound, the negatively charged atom receiving positive electricity from the positive pole, to which it is attracted, and becoming neutral; the positively charged, attracted and neutralized at the negative pole. The compound would thus necessarily be broken down by electrolysis, since the force which held its constituents together no longer exists.

**Berzelius' Electrochemical Theory.** — The theory of Berzelius differed fundamentally from that of Davy. Accord-

ing to Davy, an atom, as such, is electrically neutral, and becomes charged positively or negatively by contact with another atom, which takes a charge of the opposite sign. Berzelius claimed that every atom is electrically charged with both kinds of electricity. These exist upon the atom, in polar arrangement, and the electrical character of the atom depends upon which is present in excess. One is usually present in large excess, giving the atom a decidedly positive or negative character. One "pole" is usually much stronger than the other, so that the atom reacts as if it was "unipolar." Chemical attraction is but the electrical attraction of these oppositely charged atoms, and the intensity of the former is conditioned by the magnitude of the latter.

A negatively charged atom is attracted to and combines with one which is charged positively. The magnitude of these opposite charges may not be the same, and the compound formed will itself be electrically positive or negative, depending upon which charge upon the atoms is the greater. Two compounds, the one charged positively and the other negatively, may, then, in turn, combine, forming a still more complex compound. In this way Berzelius attempted to account for the more complex substances, such as the so-called double compounds.

The theory, as put forward by Berzelius, did not long enjoy freedom from adverse criticism. If chemical union is produced by the electrical attraction of oppositely charged atoms, then, as soon as these atoms come together, the electrical differences would disappear, and the compound must fall apart. As soon, however, as the atoms separated, they would become oppositely charged, and again reunite.

There would thus result a continued decomposition and reunion, and a chemical compound would, at best, be in a state of unstable equilibrium. This would apply to all chemical compounds.

But the theory was called upon to meet, apparently, a more serious objection. If chemical union depends only upon the attraction of the opposite electrical charges upon the atoms, then the properties of the compound formed must depend upon the nature of the charges upon the atoms in the compound. It was, however, found to be possible to substitute the three hydrogen atoms in acetic acid by three chlorine atoms, passing from $CH_3COOH$ to $CCl_3COOH$. And the remarkable fact was discovered, that the properties of trichloracetic acid were very similar to those of acetic acid itself.

This, Berzelius himself could not satisfactorily reconcile with his theory. Each of the three hydrogen atoms carried a positive charge, while the three chlorine atoms each carried a negative. Yet the three hydrogen atoms, with their positive charges, could be replaced by the three chlorine atoms with their negative charges, without materially changing the properties of the compound. This is cited, up to the present, as a fatal objection to the electrochemical theory of Berzelius.

The very recent work of J. J. Thomson[1] has, however, thrown entirely new light on the above line of argument. Thomson has shown that the same substance may be both positively and negatively charged. Thus, hydrogen gas[2] has been electrolyzed by him, with the result that positive hydrogen went to one pole and negative to the other.

[1] Nature, 52, 453. [2] *Ibid.*, 52, 451 (1895).

This was shown from the difference in the spectra of the hydrogen around the two poles. The molecule of hydrogen is, then, very probably made up of a positive and a negative hydrogen ion. [7].

The important point in this connection, brought out by the work of Thomson, is that we must not conclude that because hydrogen is sometimes positively charged, it is always so. Thomson's own words, in connection with that portion of his paper which bears on the theory of Berzelius, are here given.

"In many organic compounds, atoms of an electropositive element hydrogen are replaced by atoms of an electronegative element chlorine, without altering the type of the compound. Thus, for example, we can replace the 4 hydrogen atoms in $CH_4$, by Cl atoms, getting, successively, the compounds $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$, and $CCl_4$: it seemed of interest to investigate what was the nature of the charge of electricity on the chlorine atoms in these compounds. The point is of some historical interest, as the possibility of substituting an electronegative element in a compound for an electropositive one was one of the chief objections against the electrochemical theory of Berzelius. When the vapor of chloroform was placed in the tube, it was found that both the H and Cl lines were bright on the negative side of the plate, while they were absent from the positive side, and that any increase in the brightness of the H lines was accompanied by an increase in the brightness of those due to Cl. . . . The appearance of the H and Cl spectra on the same side of the plate was also observed in methylene chloride, and in ethylene chloride. Even when all the H in $CH_4$ was replaced by Cl, as in carbon tetra-

chloride $CCl_4$, the Cl spectra still clung to the *negative* side of the plate."

The same point was tested with $SiCl_4$, and the Cl spectra was brightest on the *negative* side of the plate. "From these experiments it would appear that the Cl atoms, in the chlorine derivatives of methane, are charged with electricity of the same sign as the H atoms they displace."

From this, the argument against the theory of Berzelius is left without foundation, since the hydrogen atoms in acetic acid are replaced by chlorine, which has the same kind of charge. Therefore, the properties of trichloracetic acid should resemble closely those of acetic acid itself.

**Faraday's Law.** — The next important advance in electrochemistry was made by Faraday, upon whose investigations too much stress cannot be laid. He showed the identity of electricity from different sources, whether produced by friction or by chemical action; and also investigated the relation between the amount of a compound decomposed by the current, and the amount of current. He found that the two were proportional to one another, and then announced his law.

The amount of chemical decomposition effected by the passage of the current is proportional to the amount of electricity which flows through the conductor.

Faraday determined, also, the amounts of different elements, which would be separated from their compounds, by passing the same current through solutions of these compounds. For example, the same current would be passed through solutions of, say, copper sulphate, zinc chloride, and silver nitrate, and the amounts of Cu, Zn, and Ag deposited determined.

The following generalization was reached by this work: —

The amounts of the different elements which are separated by the same quantity of electricity bear the same relation to one another as the equivalents of these elements.

The atoms of all univalent elements carry exactly the same quantity of electricity, — of bivalent elements twice as much, of trivalent three times, and so on. In a word, all atoms have either the same capacity for electricity, or a simple rational multiple of the capacity of the univalent atoms.

Faraday is also the author of the system of nomenclature, which we use in electrochemistry up to the present.

**Electrolysis.** — The power of the current to decompose chemical compounds had been made especially prominent by the work of Faraday. This he termed electrolysis.

Some of the most interesting and important advances made in electrochemistry, at that time, were along this line; and theories were proposed to account for the facts then known, which we now recognize to contain the germ of the theory of electrolytic dissociation. If the two poles of a voltaic cell are immersed in acidulated water, hydrogen is liberated upon the one pole, and oxygen upon the other. Between the two poles there is a layer of water particles, which apparently undergo no decomposition. The question arose, do the hydrogen and oxygen set free, come from the same or from different water particles? It is not a simple matter to answer this question satisfactorily, and yet it is fundamental to the solution of the question of electrolysis.

A superficial examination of what took place in electrolysis would probably lead to the conclusion that the hydrogen and oxygen come from different water particles. Yet it might be that the water which was decomposed was that which was exactly halfway between the poles, and that the hydrogen moved from this point in the one direction, and the oxygen in the other.

Humphry Davy undertook to answer this question experimentally. He placed the poles of a voltaic cell in separate vessels, containing acidulated water, and connected the two vessels by placing a finger of one hand in the one, and a finger of the other hand in the other, care being taken to properly insulate his body from the earth. Electrolysis took place, hydrogen separating at one pole of the battery, oxygen at the other. In such an arrangement, it is difficult to see how the oxygen and hydrogen set free could come from the same particle of water. It is, therefore, very probable, that in the electrolysis of acidulated water, the hydrogen and oxygen which are liberated at the poles come from different molecules of water.

**Theories of Electrolysis.** — The first to account at all satisfactorily for electrolysis was Grotthuss, at the early date of 1805. At the moment when the hydrogen and oxygen separate, the one becomes positive and the other negative. The positively charged hydrogen is attracted to the negative pole, and repelled from the positive pole. The negatively charged oxygen is attracted to the positive pole, and repelled from the negative. But since the attracting and repelling forces vary inversely as the square of the distance from the electrodes, the sum of the forces which act, respectively, upon the hydrogen and oxygen

particles, as they approach the electrodes, is constant. This clear and concise idea of Grotthuss is represented graphically in the accompanying figure.

The atoms marked positive represent hydrogen; those marked negative, oxygen. Before the current is passed, each oxygen atom is combined with a definite hydrogen atom, forming water. When the current is passed, the hydrogen atom nearest the negative pole gives up its positive charge to that pole, becoming electrically neutral, and separates as hydrogen gas. The oxygen atom which

FIG. 1.

was originally in combination with this hydrogen is now free, but it combines at once with the hydrogen of the next molecule of water. This sets another oxygen atom free, which combines with the hydrogen of the next water molecule, and so on until the positive pole is reached, when the last oxygen atom in the chain, not finding any hydrogen with which to combine, takes up a positive charge from the positive pole, becomes electrically neutral, and escapes as gaseous oxygen.

The gases, which escape only at the electrodes, come

from different molecules of water, as was made probable by the experiment of Davy. The layers of molecules between the electrodes are, during the electrolysis, constantly interchanging their constituents.

The distinctive feature of the theory of Grotthuss is, that before the current is passed, each hydrogen atom is combined fixedly with a definite oxygen atom, from which it never parts company. The current must first decompose the water molecules, before any electrolysis can take place. This theory accounted, satisfactorily, for all the facts which were known about electrolysis, at the time when it was proposed.

**Clausius's Theory of Electrolysis.** — While the theory of Grotthuss accounted for all the facts which were then known, new facts were soon brought to light, which could not be reconciled with it. According to this theory, the current must first decompose the molecules before it can effect any electrolysis. If the current used is not capable of decomposing one molecule of water, it is clear that it cannot decompose more than one, and no electrolysis would result. But as the strength of the current increases, it must reach a point where it is capable of decomposing a molecule of water. At this point many molecules must be simultaneously decomposed, since they are all under the effect of the same force, and have almost exactly the same position to one another. If the conductor conducts only electrolytically, we must conclude from this theory, that as long as the driving force in the conductor is below a certain limit, no current will pass; but when it has reached this limit, a very strong current suddenly exists.

Says Clausius,[1] this conclusion from the theory is in direct opposition to what are now known to be the facts. The smallest force produces a current by alternate decomposition and reunion, and the intensity of the current increases according to Ohm's law, *i.e.* proportional to the force. Therefore, the assumption that the part molecules of an electrolyte are combined rigidly to form whole molecules, and that these have a definite, regular arrangement, is without foundation.

The assumption, then, that the natural condition of an electrolytic liquid is one of equilibrium, in which every positive part molecule is combined rigidly with a negative, was abandoned by Clausius as untenable, and his own theory proposed in its place.

An electrolytic solution consists mainly of whole molecules of the electrolyte, but in addition there are some "part molecules," which have parted company. A positive part molecule may, during the movements to which it is subjected, come into a position with respect to the negative part of another molecule, which is more favorable for union with this than with its own negative companion. It would then part company with the latter, and join the former. This would have, then, a positive and a negative part molecule, each free to move about through the solution and combine with other part molecules, or break down whole molecules already existing as such in the solution. These movements and decompositions take place as irregularly as the heat movements which produce them. The two part molecules, resulting from the breaking down of a whole molecule, may combine directly with

[1] Pogg. Ann., 101, 338 (1857).

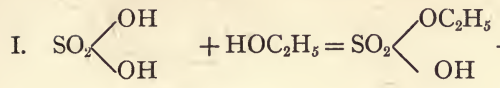
one another, or may be prevented from doing so by the movements due to heat. The amount of such decomposition in a solution would depend upon the nature of the solution and upon the temperature.

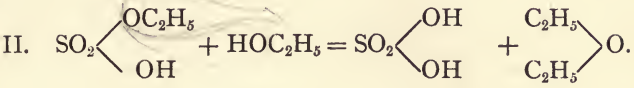
Allow an electric force to act upon a solution containing a mixture of whole and of part molecules. The part molecules will no longer move about in all directions, due to the action of heat alone, but more positive parts will move in the direction of the negative pole, and negative parts toward the positive pole, than in the other directions. This directing influence of the current will also facilitate the breaking down of the whole molecules into part molecules.

This assumption of a partial breaking down of the molecules in an electrolytic solution, before the current is passed, accounts for the fact that a weak current will effect electrolysis — a fact which could not be brought within the range of the theory of Grotthuss. The directing influence which the current exerts would exist for a current of any strength, and would be proportional to the strength of the current. In the opinion of Clausius, the action of the current is primarily a directing one, but, at the same time, it facilitates the decomposition of the molecules into part molecules. This theory of Clausius, as will be seen later, contains the germ of the theory of electrolytic dissociation.

A theory as to the condition of things in solution was proposed by Williamson[1] in 1851, as the outcome of his work on the preparation of ether by the action of sulphuric acid on ethyl alcohol. The reaction which produced the ether was recognized as proceeding in two stages: —

[1] Liebig's Ann., 77, 45 (1851).





The first stage of the reaction consists in the replacement of a hydrogen atom in the sulphuric acid, by the ethyl group, with the elimination of a molecule of water; the second, in the replacement of the ethyl group in ethyl sulphuric acid by the hydroxyl hydrogen of the alcohol. The reaction which takes place as represented in I is then almost exactly reversed in II, the final result being the removal of a molecule of water from two molecules of alcohol, and the formation of a molecule of ether. From this Williamson concluded, "that in an aggregate of the molecules of every compound, a constant interchange between the elements contained in them is taking place."

He concluded his paper with this statement: "In recent years chemists have added to the atomic theory an uncertain, and, as I believe, an unsubstantiated hypothesis, that the atoms are in a condition of rest. I reject this hypothesis, and found my views on the broader basis, the *movement* of the atoms."[1]

Clausius criticised the views of Williamson as being too broad. His assumption went too far beyond the facts. It was not necessary to assume that all, or even a large part, of the molecules in a solution are broken down into part

[1] Liebig's Ann., 77, 48.

molecules. The assumption that a few of the molecules are thus broken down, accounted for all the facts then known.

**Hittorf's Work on the Migration Velocity of Ions.** — The changes in concentration, which take place when solutions are electrolyzed, could be explained only by assuming that the positive and negative part molecules, or, as Faraday called them, ions, move through the solution with different velocities. The measurement of these relative velocities was undertaken by Hittorf,[1] and his investigation of this problem has now become a classic. He studied the effect of concentration of solution, temperature, and strength of current, upon the relative velocities of ions. His work is of importance, not simply as giving us the relative velocity of ions, but as throwing light on a number of other problems. What ions are formed from the given compounds? which constituents go to make up the cation, and which the anion? are questions which come within the range of the work of Hittorf. Take the compound $K_2PtCl_6$; does the platinum form part of the cation, or of the anion? does it go to the positive or to the negative pole? Or take the compound $K_4Fe(Cn)_6$; when it is electrolyzed, does the iron go with the potassium to the cathode, or with the cyanogen to the anode? The solution of such problems is of great assistance in determining the chemical constitution, especially of complex compounds.

**Kohlrausch's Work on the Conductivity of Solutions.** — Solutions of different electrolytes show very different conducting power. A simple and accurate method of meas-

[1] Pogg. Ann., 89, 117, 177; 98, 1; 103, 1; 106, 337, 513.

uring the conductivity of solutions has been devised by Kohlrausch.[1] He has applied his method to a large number of solutions of different concentrations of acids, bases, and salts; and has furnished us with the most accurate conductivity measurements which have ever been made. The results of this work will be considered in a later chapter, since their bearing upon the theory of electrolytic dissociation is direct. Indeed, we shall learn that the conductivity of solutions of electrolytes furnishes us with one of the most rigid tests to which the theory of electrolytic dissociation can be subjected.

## THE DEVELOPMENT OF CHEMICAL DYNAMICS AND CHEMICAL STATICS

The brief sketch which will be given here, of the development of this branch of physical chemistry, will not include the earliest suggestions to account for chemical action, since many of them are now only of historical interest. The Swedish chemist, Bergmann, attempted generalizations which were undoubtedly advances on the disconnected knowledge before his time; but it was Wenzel (1777) who first saw clearly the effect of mass on chemical action, and laid the foundation for the law of mass action, which has played such a prominent rôle since his time. He, however, gave only a qualitative expression to the law; viz., that chemical action is proportional to the concentration of the substances which are allowed to react.

Berthollet developed much more fully the effect of

[1] Pogg. Ann., 138, 280; 154, 1; 159, 233; Wied. Ann., 6, 1; 11, 653; 26, 161.

mass in chemical action, and showed by direct experiment how it comes into play. The affinities which exist between substances are not to be regarded as absolute forces, but are dependent upon the masses of the substances which are present. Thus barium sulphate can be partly decomposed by boiling it with potassium hydroxide. Calcium oxalate can, similarly, be partly decomposed by the same reagent. If the potassium hydroxide is present only in small quantity, no appreciable decomposition takes place; but if the quantity is large, and is removed from time to time, new alkali being added, barium sulphate can be completely decomposed by boiling potassium hydroxide. This was a clear demonstration of the effect of mass.

Following this same idea, Berthollet pointed out the effect of the state of aggregation on chemical activity. That chemical activity should be greatest, it is necessary that all the parts should come into action. This is best effected in the liquid state of aggregation. If a solid is present, the activity is less, or if a solid is formed as the result of the reaction, its activity is far less than in the liquid condition. Similarly, if a gas is formed in the reaction, it quickly escapes from the field of action, and its chemical activity therefore ceases.

This work of Berthollet was published in two volumes as his "Essai de Statique Chimique," but was so far in advance of its day, that it either failed to attract attention altogether, or only aroused opposition from those who did not comprehend its full significance.

It was much later before any further evidence was brought forward, to show the effect of mass in chemical

activity. Heinrich Rose[1] showed that the sulphides of the alkaline earths are largely decomposed when boiled with large volumes of water, liberating hydrogen sulphide, and forming the hydroxide.

He also called attention[2] to a process which is going on in nature. Over the surface of the earth the weak chemical reagents, carbon dioxide and water, are continually decomposing some of the most stable compounds — the silicates. The geological process known as weathering is a replacement of silicates by hydroxides and carbonates, or by basic carbonates. This reaction, in which such stable compounds are broken down by such a weak acid as carbonic acid, requires, of course, a long period of time, and is the result of the mass action of a large amount of carbon dioxide, such as exists in the atmosphere, and in the soil. Such a reaction is entirely beyond the possibilities of the laboratory, on account of the time and mass of substance required to effect it.

Rose[3] also carried out some investigations on the decomposition of insoluble salts by soluble salts. It was known, long before his time, that barium sulphate can be transformed into the carbonate, both by fusion with potassium carbonate, and also by boiling with an aqueous solution of potassium carbonate. Rose, however, undertook a quantitative study of the conditions under which this transformation takes place, and the amount of carbonate required to effect complete decomposition. He found that the sulphates of strontium and calcium are more easily decomposed by alkaline carbonates than the sulphate of barium,

[1] Pogg. Ann., 55, 415. [2] *Ibid.*, 82, 545.
[3] *Ibid.*, 94, 481; 95, 96, 284, 426.

and concluded, correctly, that this was due to the presence of a reversible reaction between the barium carbonate and alkaline sulphate formed, resulting in the reformation of barium sulphate.

The result of this work of Rose, and that of his contemporaries, was to call attention to the rôle played by mass in bringing about chemical reaction. The full importance of the action of mass, as we shall see, was, however, not recognized until somewhat later.

**Wilhelmy's Discovery of the Law of Reaction Velocity.** — Wilhelmy [1] treated cane-sugar with a number of acids, and studied the velocities with which inversion takes place. He worked with different acids, with different amounts of cane-sugar, and at different temperatures. He found that it was only the sugar which underwent change, the acid remaining unaltered. The law of mass was found to obtain; the amount of sugar transformed in a given time being proportional to the amount present at that time.

Applying the principle of mass, — remembering that it is only the sugar which undergoes change, the acid being unaltered, — Wilhelmy deduced the following mathematical relations, which are taken from his epoch-making paper: [2] —

"Let $dZ$ be the amount of sugar inverted in unit time $dT$, and let us assume that this is determined by the formula: [1] —

$$-\frac{dZ}{dT} = MZS$$

in which $M$ is the mean value of the infinitely small quantity of sugar, which is transformed in unit time, by the

[1] Pogg. Ann., 81, 413 (1850). [2] *Ibid.*, 81, 418.

action of the unit of acid present. ($Z$ is the amount of the sugar, $S$ that of the acid.)

"The above equation gives, on integration:—

$$\text{Log } Z = -\int_0^T MSdT$$

or since, as already shown, $S$ is constant, $M$ is also independent of $Z$, and at the same time from $T$, which should be proved later by experiment:—

$$\text{Log } Z = -MST + C.$$

For $T = 0$, $Z = Z_0$, whence:

$$\text{Log } Z_0 - \log Z = MST, \text{ or } Z = Z_0E.$$

Since $Z_0$, $S$, and $T$ are given, and $Z$ is known by experiment, the formula can be used to determine $M$."

This work of Wilhelmy, which must be regarded as the foundation of chemical dynamics, like most important investigations, did not receive a just recognition until attention was called to it much later.[1] When we consider that this was the first successful attempt to express the velocity of a chemical reaction mathematically, and that this was in 1850, we can form some conception of the rapidity of the growth of knowledge along this line.

Other contributions to our knowledge of the mechanism of chemical reactions were made in the next few years. Löwenthal and Lenssen[2] showed that the amount of sugar inverted by different acids was proportional to the strength of the acids. But the next marked advance we owe to the French chemist Berthelot.

[1] Ostwald, Journ. prakt. Chem., 29, 385 (1884).
[2] Journ. prakt. Chem., 85, 321 (1852).

**Work of Berthelot and Péan de St. Gilles.** — Berthelot and Péan de St. Gilles[1] made an elaborate investigation of the conditions of formation and decomposition of ethereal salts. The reactions by which these are formed from acids and alcohols proceed slowly, and tend toward a limit, the point at which the reaction reaches a condition of equilibrium depending upon the amount of acid or alcohol present, upon the temperature, etc. On the other hand, if an ethereal salt is treated with water, a certain amount of it is decomposed, the amount depending upon the quantity of water used, and other conditions. A reaction of this kind is, evidently, well adapted to the study of reaction velocity, condition of equilibrium, etc.

They determined the effect of temperature on the velocity of this reaction, and found that to transform 30 per cent of a given mixture of alcohol and acid, at from 6° to 9°, required 95 days, while at 100° it required less than 5 hours to effect the same transformation. Pressure was also found to have an influence on reaction velocity, at least up to sixty or eighty atmospheres.

Berthelot[2] and St. Gilles, in the course of their study of ether formation, arrived at the following generalization: "The amount of ether formed in every moment is proportional to the product of the reacting substances." This was a beautiful confirmation of the action of mass.

They also determined the relation between chemical composition and the amount of ether formed. A few of their results are given, using different alcohols and acids, and allowing the reaction to proceed until equilibrium was

[1] Ann. Chim. Phys. [3], 65, 385; 66, 5; 68, 225 (1862–1863).
[2] *Ibid.* [3], 68, 225.

reached, *i.e.* until the maximum amount of ether was formed under the conditions. This is indicated in percentage of the theoretical amount of ether which might be formed under the conditions, if the reaction went to the end.

| | Limit |
|---|---|
| $C_2H_6O$ with $CH_3COOH$ | 66.9% |
| $C_2H_6O$ with $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$ | 69.8% |
| $C_2H_6O$ with $C_6H_5COOH$ | 67.0% |
| $CH_4O$ with $CH_3COOH$ | 67.5% |
| $CH_4O$ with $C_6H_5COOH$ | 64.5% |
| $CH_4O$ with $C_2H_4(COOH)_2$ | 66.1% |
| $C_5H_{12}O$ with $CH_3COOH$ | 68.9% |
| $C_5H_{12}O$ with $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$ | 70.7% |
| $C_5H_{12}O$ with $C_6H_5COOH$ | 70.0% |

This is a remarkable result. Neither the chemical composition of the acid, nor of the base, has any marked influence on the amount of ether formed.

The effect of increasing the amount of the alcohol, with respect to the acid, was also determined.

$n$ is the number of equivalents of ethyl alcohol, to one equivalent of acetic acid.

| $n$ | Limit | $n$ | Limit | $n$ | Limit |
|---|---|---|---|---|---|
| 0.2 | 19.3% | 2. | 82.8% | 12.0 | 93.2% |
| 0.5 | 42.0% | 4. | 88.2% | 19.0 | 95.0% |
| 1.0 | 66.5% | 5.4 | 90.2% | 50.0 | 100.0% |
| 1.5 | 77.9% | | | | |

These results exhibit the effect of mass in a striking manner; all the acid being transformed into ethereal salt, when fifty equivalents of alcohol are present to one of acid.

The action of mass was shown also by the work of

Deville [1] on dissociation. Many substances are partially broken down by heat into their constituents — in many cases into their elements. Thus, water-vapor at a high heat is partially decomposed into hydrogen and oxygen. The fact was established, that if either the hydrogen or oxygen resulting from the decomposition is removed, the dissociation will proceed farther, and may become complete. If, on the other hand, an excess of either hydrogen or oxygen is added to the dissociating water-vapor, the amount of dissociation is decreased. Deville studied a number of cases, and concluded that this is general, that an excess of either of the products of dissociation will diminish the amount of dissociation of a vapor. An excellent example of this is furnished by phosphorus pentachloride. This compound cannot be volatilized without decomposition, unless there is an excess of either chlorine or phosphorus trichloride present. In the presence of an excess of one of these, the molecular weight of phosphorus pentachloride, as determined, is very close to the theoretical molecular weight.

This work of Deville is one of the most direct confirmations of the effect of mass, yet it was used by him as an argument against mass action, being a factor in chemical activity. Another example of admirable work, but erroneous interpretation of results obtained.

**Guldberg and Waage's Law of Mass Action.** — We have seen that the effect of mass on chemical activity was recognized as early as the time of Wenzel. A clearer expression of its action was furnished by Berthollet. Rose showed, both from nature, and by direct experiment, what

[1] Compt. rend., 45, 857; 56, 195, 729; 59, 873; 60, 317.

a marked influence mass has in effecting chemical reactions. Berthelot and Péan de St. Gilles demonstrated the effect of mass action on the formation of ethereal salts from alcohols and acids, and thus made it probable that the effect of mass on chemical reactions is general.

It was Guldberg and Waage,[1] however, who gave a complete mathematical expression to the action of mass. If two substances react, the action is proportional to the active masses of each of them. The intensity of the reaction is, therefore, measured by the product of the active masses. The reaction is, of course, dependent also upon the nature of the substances, temperature, etc. These must be taken into account. If we represent the active masses of two substances by $m$ and $n$, and the coefficient depending upon the nature of the substance, etc., by $c$, the force of the chemical reaction is expressed by $mnc$.

If the reaction is reversible, *i.e.* if the substances formed can react and give the original substances, as *e.g.* in the formation of ethereal salts, then there will exist a force which tends to stop the original reaction, and to set up one in exactly the opposite sense. If we represent the active masses of the substances formed in the original reaction by $m'$ and $n'$, and the coefficient depending upon the nature of the substances by $c'$, the magnitude of the force opposing the original reaction will be expressed by $m'n'c'$.

When the condition of equilibrium is reached, the two forces are equal and opposite, and we have:—

$$mnc = m'n'c'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1] Études sur les Affinités Chimiques, Christiania, 1867; Journ. prakt. Chem. [2], 19, 69 (1879). Ostwald's Lehrb. d. allg. Chemie, II, 2, p. 104.

If we bring together equivalents of the four substances $m$, $n$, $m'$, $n'$, they will generally not be in a state of equilibrium, but a certain amount of $m$ and $n$ will pass over into $m'$ and $n'$, and this amount we will call $x$. The amounts of the four substances present will then be, $m - x$, $n - x$, $m' + x$, $n' + x$. The active masses being the amounts in a given volume $v$, we will have: —

$$\frac{m-x}{v}, \quad \frac{n-x}{v}, \quad \frac{m'+x}{v}, \quad \frac{n'+x}{v},$$

where $v$ is the entire volume of the solution. Substituting these values for $m$, $n$, $m'$, and $n'$ in (1), we have: —

$$(m-x)(n-x) = \frac{k'}{k}(m'+x)(n'+x).$$

This equation is perfectly general, applying to all values of $x$. If we determine $x$ in any one case, we can calculate $\frac{k'}{k}$. Knowing $\frac{k'}{k}$, we can calculate the value of $x$ for any amounts of the original substances brought together. In a word, we could calculate exactly how the four substances would react, whatever the quantities brought together, and how much of each would exist when equilibrium was reached.

Guldberg and Waage's work also led to a more comprehensive conception of the reversibility of many chemical reactions, equilibrium being the special condition under which the reactions in the two directions were of equal velocity. The velocity of any reaction is, in reality, the difference between the velocity in one direction, and the velocity in the other. The velocity $v$ is the amount transformed in unit time, $v = \frac{dx}{dT}$; but this is equal to a

factor $\theta$ times the force acting in one direction, minus the force acting in the other direction.

$$v = \frac{dx}{dT} = \theta(mnc - m'n'c').$$

If the reaction proceeds only in one direction, $m'n'c'$ becomes equal to zero, and the equation of reaction velocity becomes: —

$$v = \frac{dx}{dT} = \theta(mnc).$$

The above relations obtain, only when all of the substances which enter into the reaction are soluble. If one or more of the substances is insoluble, the relations are much simplified. Take the reaction between potassium carbonate and barium sulphate, in which potassium sulphate and barium carbonate are formed.

Let $M$ be the active mass of potassium carbonate.

Let $N$ be the active mass of barium sulphate.

Let $M'$ be the active mass of potassium sulphate.

Let $N'$ be the active mass of barium carbonate.

Barium sulphate and barium carbonate are insoluble, and their active masses, $N$ and $N'$, are, therefore, constant. We have then: —

$$MC = M'C' \text{ or } \frac{M}{M'} = \text{constant.}$$

This is a very simple relation, and holds whenever two of the substances are insoluble. The value of the constants for the insoluble substances depends upon their degree of insolubility.

The law of mass action has been tested in a large number of directions, and by a great variety of methods. The

general result has been a thorough confirmation of the views of Guldberg and Waage.

**The Application of Thermodynamics to Chemical Processes.** — The scope of this work will not permit of more than a brief reference to the leading investigations bearing upon this problem. Horstmann[1] was the first to successfully apply thermodynamics to chemical processes. He chose dissociation phenomena, since they are reversible processes; and if they take place between solids and gases, obey the same laws as vaporization. If we represent by $h$ the heat of combination, and by $p$ the dissociation pressure, the following relation between the two obtains: —

$$h = Tu \frac{dp}{dT}$$

in which $T$ is the absolute temperature, and $u$ the volume of the vapor. Knowing either $h$ or $p$, we can calculate the other. He later applied the entropy principle to conditions of equilibrium, and showed that a system will always assume that arrangement in which entropy is a maximum. The condition for equilibrium is then: —

$$\frac{de}{dx} = 0,$$

in which $e$ is the entropy, and $x$ the amount of untransformed substance.

Willard Gibbs's[2] applications of thermodynamics to conditions of chemical equilibrium are so comprehensive and general, that it is impossible to give any adequate concep-

[1] Ber. d. chem. Gesell., 2, 137; 4, 635; Liebig's Ann., 170, 192 (1872-1873).

[2] Trans. Conn. Acad., III, 1874-1878. Translated into German by Ostwald, Leipzig, 1892.

tion of his epoch-making work in a few paragraphs. The reader who may desire to follow out Gibbs's mathematical deductions must be referred to his original communication, or to the second part of the second volume of Ostwald's Lehrbuch, where a systematic account of his deduction is given.

It should, however, be stated here, that the work of Willard Gibbs has placed the science of chemical equilibrium on an entirely new basis, from the theoretical standpoint, and is ranked as one of the leading contributions to mathematical chemistry and physics.

The work of van't Hoff[1] is in part theoretical, and in part experimental. This deals largely with the velocity of reactions from both standpoints, and also investigates the influences which affect the velocity of a reaction, such as temperature, pressure, form of vessel, etc. The conditions of equilibrium were also investigated by van't Hoff and his pupils, and the temperatures ascertained at which a large number of transformations take place.

The observations for the different kinds of equilibrium have led to the following general conclusion:[2] "Every equilibrium between two different conditions of matter (systems) is, at constant volume, by a decrease in temperature, displaced in the sense of that system whose formation liberates heat." This generalization includes all possible cases of chemical as well as of physical equilibrium. This principle, termed by van't Hoff that of "movable equilibrium," is then applied to both heterogeneous and

[1] Études de Dynamique Chimique, Amsterdam, 1884. Studien zur Chemischen Dynamik, van't Hoff and Cohen.

[2] Studien zur Chemischen Dynamik (van't Hoff and Cohen), p. 223.

homogeneous equilibria. The concluding chapter of this important work by van't Hoff and Cohen is devoted to the subject of chemical affinity. The generalization reached was,[1] that "the work expressed in calories, which affinity can do in a chemical transformation, at a given temperature, is equal to the amount of heat which this transformation produces, divided by the absolute temperature at which the transformation takes place, and multiplied by the difference between this, and the temperature at which the transformation takes place."

If $A$ is the amount of work done, $q$ the amount of heat produced, $T$ the temperature of the transformation, and $P$ the absolute temperature of the transformation, we have: —

$$A = q\left(\frac{P-T}{P}\right),$$

which is the mathematical expression of the above generalization. In connection with the study of chemical equilibrium, the work of Le Chatelier[2] must be mentioned. He arrived at two laws which he stated thus: Law of the opposition of action and reaction (page 210). "Every variation of a factor of equilibrium causes a transformation of the system, which tends to make the factor in question undergo a variation of sign opposite to that which we have given it."

Thus, an elevation of temperature produces a reaction with absorption of heat, an increase in pressure a reaction with diminution of volume, etc.

[1] Studien zur Chemischen Dynamik, p. 247.

[2] Recherches Expérimentales et Théoriques sur les Équilibres Chimiques. Paris, 1888.

Le Chatelier termed his second generalization the law of equivalence of systems in equilibrium, and expressed it thus: —

"Two equivalent elements in a system in equilibrium, *i.e.* which can be substituted for one another without changing the condition of equilibrium, will be equivalent in every other system where they can be substituted for one another, and further, will be mutually in equilibrium if in opposition to one another."

An example cited is the equality of the vapor-tension of water and of ice at the melting-point.

**Methods of measuring Affinity.** — The theoretical deductions, especially of the last four pieces of work referred to, have been tested experimentally by a number of methods. Julius Thomsen[1] determined the way in which a base is divided between two acids, by means of the amount of heat liberated. While Ostwald,[2] utilizing the change in volume which occurs in chemical reactions, obtained far more satisfactory and reliable results than Thomsen. Ostwald showed that the action between acids and bases is conditioned by two coefficients, the one depending upon the nature of the acid, the other upon the nature of the base. The chemical affinity of an acid for a base is then expressed by the product of these two coefficients. These affinity coefficients are the numerical expressions of the strength of the acid or base, and hold, quantitatively, for all actions in which the acid or base takes part.

In addition to the thermochemical method of J. Thomsen, and the simpler and more reliable volume chemical

[1] Pogg. Ann., 138, 497 (1869).
[2] Journ. prakt. Chem. [2], 16, 385 (1877).

method of Ostwald, a number of other methods of measuring relative affinities have been devised. Ostwald[1] proposed the velocity with which substances like zinc sulphide, or calcium oxalate, are dissolved by different acids, as a measure of the relative affinities of the acids. He[2] also used the velocity, with which a reaction like the transformation of acetamid into ammonium acetate takes place under the influence of acids, as a measure of the affinities of the acids. Ostwald has also studied other reactions in this same connection, such as the catalysis of methyl acetate, inversion of cane-sugar, etc., and found that the coefficients for the different acids, as determined by the different methods, agreed satisfactorily.

A relation was thus discovered, which, as we will see, is of the very greatest importance, in connection with the theory of electrolytic dissociation. The affinity coefficients of acids and bases bear the same quantitative relations to one another as the conductivities of these acids and bases.

The discussion of this relation belongs to a later chapter of this work, and it suffices here to merely call attention to its existence.

**Conclusions from the Earlier Physical Chemical Work.** — From the preceding sketch of the development of the several chapters of physical chemistry, we can form a fairly clear conception of the state of physical chemistry just before the theory of electrolytic dissociation was proposed. Much work had been done on the relations between the various properties, and composition and constitution; and a great number of generalizations had been reached, which, however, held only approximately. Much

[1] Journ. prakt. Chem. [2], 19, 468 (1879). [2] *Ibid.* [2], 27, 1 (1883).

valuable experimental work had also been done on the amount of heat liberated in chemical reactions, laying stress upon the energy transformations which take place in chemical processes, and which are probably the conditioning causes of all chemical action. Here, also, relations were pointed out, which, however, like the above, have been shown to be only approximations. Then, the foundations of electrochemistry were laid, early in the century, and rapidly developed, and theories to refer chemical action to purely electrical causes were proposed. The decomposing action of the current was studied, and theories advanced to explain electrolysis, which lie at the foundation of our most modern theory. The relation pointed out here by Faraday, between the amount of current and the amount of decomposition which it effects, is one of the most exact with which we have to deal. Similarly, other electrochemical relations are freer from exceptions than those which we have just considered. Some of the more important steps in the development of chemical dynamics and statics have been taken up, including, especially, the law of mass action, which underlies this entire chapter of physical chemistry.

But, from what has preceded, we can see not only the state of development, but also the inherent nature of physical chemistry. What was the chief aim of the physical chemist in these earlier periods? It was, plainly, to discover relations between apparently disconnected phenomena and disconnected facts. It attempted to connect, and thus systematize, the great masses of isolated facts, which were yearly being brought to light, and thus refer them, as far as possible, to common causes.

It has, however, been repeatedly shown, that these earlier relations were, in many cases, only approximations. The number of exceptions continued to increase, as more accurate experimental work was done, until, in some cases, the generalization almost entirely disappeared. Nevertheless, the aim of the earlier physical chemist is the aim of the physical chemist of to-day — to discover generalizations wherever they exist. It is by this means, and this means only, that chemistry can be advanced from pure empiricism to the rank of an exact mathematical science.

We will now follow the rise and development of the widest and most important generalization which has ever been reached by physical chemistry.

# CHAPTER II

## THE ORIGIN OF THE THEORY OF ELECTROLYTIC DISSOCIATION

### PFEFFER'S OSMOTIC INVESTIGATIONS

**Introduction.** — If we would trace the origin of the theory of electrolytic dissociation, we must turn neither to chemistry nor to physics, but to the osmotic investigations of the botanist, W. Pfeffer.[1] It had long been known, that when a solution of a substance is placed upon one side of a partition, through which the solvent can pass but the dissolved substance cannot, and the pure solvent placed upon the other side, the pure solvent will flow through the partition into the solution. This phenomenon is termed osmosis, and the pressure thus produced, osmotic pressure. We may demonstrate this phenomenon by filling a bladder with a solution of alcohol in water, and then immersing it in pure water. Water will flow through the bladder into the solution of alcohol, and the bladder will become distended. This is, of course, but a qualitative demonstration; and were we dependent upon natural membranes alone to measure osmotic pressure, it is safe to say that very little would have been accomplished. Pfeffer, however, succeeded in devising artificial membranes, with which he could study osmotic pressure quantitatively.

[1] Osmotische Untersuchungen, Leipzig, 1877; Harper's Science Series, IV, p. 3.

**Pfeffer's Method of measuring Osmotic Pressure.** — Certain precipitates have the property of allowing the solvent to pass through them, but of preventing the dissolved substance from passing. If these precipitates are deposited at the plane of contact of two solutions, or of a solution and a solvent, they act like the animal membrane described above. This important fact was discovered by Traube, who was the first to prepare these artificial membranes, and use them to study osmotic pressure. His method, however, was far inferior to that devised by Pfeffer.

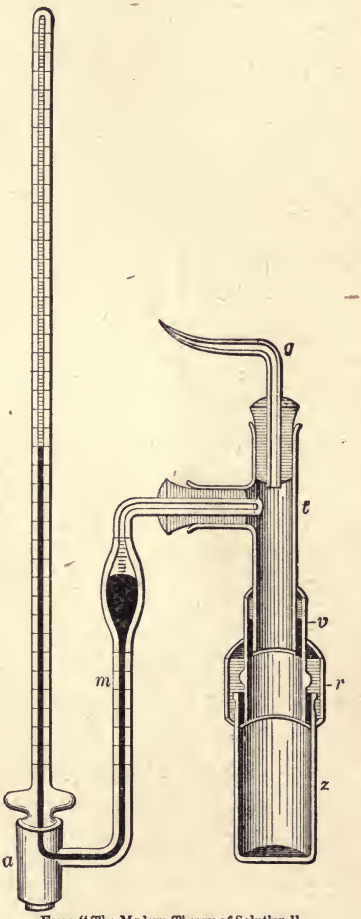
To make these membranes more resistant, Pfeffer determined to form them upon a support. He states that the plant cell furnished him with a model. "In these, the plasma membrane which, in its diosmotic properties, is similar to the artificially precipitated membranes, is pressed against the cell wall." Pfeffer caused the precipitate to be deposited in the walls of very fine-grained, unglazed porcelain cells. The precipitate which gave him the best results was copper ferrocyanide. A porcelain cell was filled on the inside with a solution of potassium ferrocyanide, and immersed in a solution of copper sulphate. The two solutions penetrated the walls of the porcelain cell, and met right in the walls.

Where they came in contact, there was precipitated copper ferrocyanide as a membrane, which, when the cell was broken, appeared as a fine line.

The membranes deposited in this way had many of the properties desired. They were semipermeable, *i.e.* allowed the solvent to pass through and prevented the dissolved substance, and were sufficiently resistant to

withstand considerable pressure without breaking. The apparatus in its complete form, as used by Pfeffer, is seen in Fig. 2.

The porcelain cell, with semipermeable membrane deposited in the walls, is seen at *z*. This cell was about 46 mm. high, 16 mm. internal diameter, and the walls were from $1\frac{1}{4}$ to 2 mm. thick. "The narrow glass tube *v*, called the connecting piece, was fastened into the porcelain cell with fused sealing-wax, and the closing piece *t* was set into the other end of this tube in the same manner. The shape and purpose of this are shown in the figure. The glass ring *r* was necessary only in experiments at higher temperature, in which the sealing-wax softened. The ring was then filled with pitch, which also held together firmly the pieces inserted into one another." The manometer *m* is attached for measuring the pressure.




From "The Modern Theory of Solution," Copyright, 1899, by Harper & Brothers.

FIG. 2.

To give an idea of the precautions which are necessary

to prepare, successfully, such semipermeable membranes as were used by Pfeffer, a paragraph is quoted from his monograph :[1] —

"The porcelain cells were first completely injected with water under the air-pump, and then placed for at least some hours in a solution containing 3 per cent of copper sulphate, and the interior was also filled with this solution. The interior only of the porcelain cell was then once rinsed out quickly with water, well dried as rapidly as possible by introducing strips of filter paper, and after the outside had dried off, it was allowed to stand some time in the air until it just felt moist. Then a 3 per cent solution of potassium ferrocyanide was poured into the cell, and this immediately reintroduced into the solution of copper sulphate.

"After the cell had stood undisturbed for from twenty-four to forty-eight hours, it was completely filled with the solution of potassium ferrocyanide, and closed as shown in Fig. 2. A certain excess of pressure of the contents of the cell now gradually manifested itself, since the solution of potassium ferrocyanide had a greater osmotic pressure than the solution of copper sulphate. After another twenty-four to forty-eight hours the apparatus was again opened, and generally a solution introduced which contained 3 per cent of potassium ferrocyanide, and $1\frac{1}{2}$ per cent of potassium nitrate (by weight), and which showed an excess of osmotic pressure of somewhat more than three atmospheres."

The osmotic pressure of solutions is measured with this apparatus as follows: The cell is completely filled

[1] Harper's Science Series, IV, p. 6.

with the solution and then tightly closed. The solution also extends into the arm of the manometer attached to the cell. The whole apparatus is then immersed in the pure solvent, as shown in Fig. 3.

The closed cell is fastened to a glass rod, and so immersed in the liquid in the bath that the entire manometer is covered. The temperature of the bath is read by thermometers. The entire apparatus is placed under a bell-jar and kept in a room at uniform temperature. This is necessary, since considerable time is required for the mercury to reach the highest point and remain perfectly stationary. Water flows in through the semi-permeable membrane, and the pressure produced is finally read off on the manometer. The water which enters the cell dilutes the solution and diminishes its osmotic pressure, but the amount

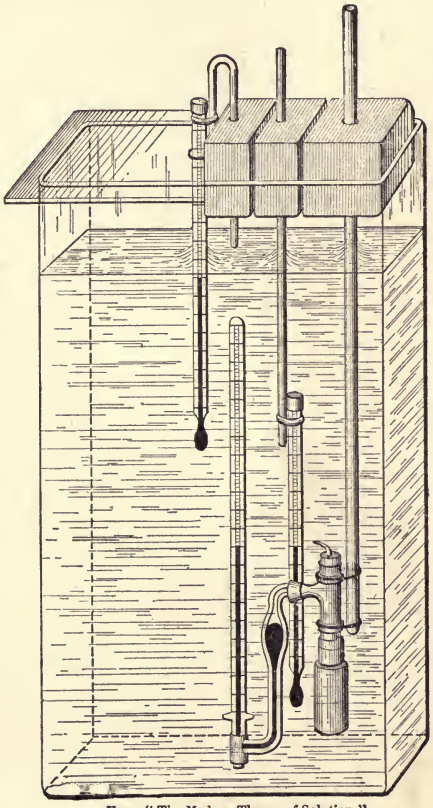


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FIG. 3.

of water which enters is so slight that the error from this source is not large.

**Some of Pfeffer's Results.** — Pfeffer measured the osmotic pressure of solutions of a number of substances at different concentrations, and at different temperatures. A few of the results which he obtained are given.

*Osmotic Pressure for Cane-Sugar of Different Concentration*

| Percentage Conc. by Weight | Osmotic Pressure |
|---|---|
| 1.0 | 535 mm. |
| 2.0 | 1016 mm. |
| 2.74 | 1518 mm. |
| 4.0 | 2082 mm. |
| 6.0 | 3075 mm. |

*Effect of Temperature on Osmotic Pressure*

The following results were obtained with a 1 per cent solution of cane-sugar: —

| Temperature | Pressure |
|---|---|
| 14.2° C. | 510 mm. |
| 32.0° C. | 544 mm. |
| 6.8° C. | 505 mm. |
| 13.7° C. | 525 mm. |
| 22.0° C. | 548 mm. |
| 15.5° C. | 520 mm. |
| 36.0° C. | 567 mm. |

These are a very few of the results which were recorded by Pfeffer.

This investigation was undertaken by Pfeffer purely from the standpoint of vegetable physiology, and with no

idea of throwing light on any physical-chemical problem. His work was completed and published in 1877. From the botanical standpoint it was a contribution of the very highest value. Pfeffer did not point out any bearing which his results might have on problems such as those with which we are now about to deal. Indeed, their significance was not seen until nearly ten years later, when van't Hoff showed that this work of Pfeffer marked the beginning of a new era in physical chemistry.

### RELATIONS BETWEEN OSMOTIC PRESSURE AND GAS PRESSURE DISCOVERED BY VAN'T HOFF

**Historical.** — In following up the discovery of a great generalization, it is always of interest to trace the stages by which it was reached. We are very fortunate in this case, since van't Hoff himself has given us an account of the development of the ideas which led him to the discovery of the relations between osmotic pressure and gas pressure. In the winter of 1894, he was invited by the German Chemical Society to give a lecture on his physical chemical investigations. He chose for his theme, "How the Theory of Solutions Arose," and here we find a detailed statement of the steps which led to his discovery. This lecture is published in full in the *Berichte der deutschen chemischen Gesellschaft*, **27**, 6 (1894). A few pages from this lecture are given, since it contains a concise statement of the facts which are of such unusual interest in this connection.

"It was when I first began to think on chemical matters, under the guidance of Kekulé and Wislicenus, that the ideas about the position of atoms in space began to germinate.

"The entire 'Arrangement of Atoms in Space' was, indeed, only a structure which depended upon the relation of a physical property — optical activity — to chemical constitution.

"Although so young, I wished then to know, also, the relations between constitution and chemical properties. The constitution formula should, indeed, be the expression of the entire chemical behavior.

"Thus arose my 'Ansichten über die organische Chemie,' with which, indeed, you are not familiar, and which is scarcely worth knowing. It had this value, however, for me, that it pointed out, very clearly, the existence of a gap.

"Let us take an example: —

"It is known that oxygen in organic compounds has an accelerating action on almost all transformations. The oxidation of $CH_4$ is more difficult than of $CH_3OH$, etc.

"To obtain relations of value in this connection, there is need of accurate knowledge of the velocity with which a reaction proceeds, and thus I began the study of the velocity of reactions, and there appeared my 'Études de Dynamique Chimique.'

"Reaction velocity was at first the chief aim, but chemical equilibrium was closely associated with it. Equilibrium resting, on the one hand, on the equality of two opposite reactions, and procuring a firm support, on the other, through its connection with thermodynamics. You see how, to obtain my object, I was ever led farther from it, which often occurs.

"And I must go still farther; for the question of equilibrium borders directly on the problem of affinity, and I was thus concerned with the very simple affinity phenomenon

— at first with that which expresses itself as an attraction for water.

"Mitscherlich had already raised the question, in his 'Text-book of Chemistry' (4th edition, 1844, 565), as to the magnitude of the attractive force which holds the water of crystallization in Glauber salts. He saw a means of measuring this in the diminished tension of the water of crystallization.

"'If Glauber salt is brought into the barometric vacuum at 9°, the mercury falls about $2\frac{1}{2}$ lines (5.45 mm.), due to the liberation of water-vapor. Water itself produces, on the other hand, a fall of 4 lines (8.72 mm.). The affinity of the sodium sulphate for its water of crystallization corresponds, therefore, to the difference, $1\frac{1}{2}$ lines (3.27 mm.), *i.e.* about $\frac{1}{32}$ kg. per square inch.'

"This value, $\frac{1}{200}$ of an atmosphere, appeared to me as small without precedent, for I had the impression that even the weakest chemical forces are very large, as appeared to me to follow also from Helmholtz's Faraday Lecture. Thus, the question arose, whether it is not possible, in simpler cases, to measure this attraction for water in a more direct way; and for this purpose the aqueous solution is the simplest conceivable — much simpler than the compound containing water of crystallization.

"Coming from the laboratory with this question vividly in mind, I met my colleague De Vries and his wife. He was just at that time carrying out osmotic investigations, and he told me about Pfeffer's determinations.

"You recognize the apparatus sketched here. The so-called osmotic pressure is measured with a battery cell, whose wall is made semipermeable, *i.e.* permeable only

to water, but not to the dissolved substance, *e.g.* sugar — by the method of Traube. This is accomplished by depositing a membrane of copper ferrocyanide within the walls of the porcelain cell. The osmotic pressure of a one per cent solution of cane-sugar is two-thirds of an atmosphere.

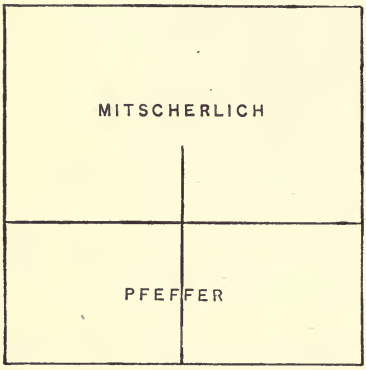


FIG. 4.

"This pressure was remarkably large in comparison with that described by Mitscherlich, and yet a relation exists between the two.

"Let us consider the sugar solution as placed below, on the left side, and separated by means of a semipermeable membrane from water which is on the right side below. The movement of the water is to the left, into the space containing vapor with the pressure observed by Mitscherlich, into the water with that observed by Pfeffer.

"A calculation can be based directly upon this relation. The force described by Mitscherlich is very small, because it acts on the more dilute vapor; that of Pfeffer is large, because it acts on the concentrated water. Therefore: —

$$\text{Pfeffer : Mitscherlich} = 1000 : \frac{P}{760} 0.08956 \frac{18}{2} \left(1 + \frac{1}{273} t\right),$$

and thus Pfeffer's force, calculated from the decrease in tension (freezing-point): —

| Temperature | Osmotic Pressure | $0.00239\,T$ |
|---|---|---|
| 6.8° | 0.664 | 0.668 |
| 15.5° | 0.684 | 0.689 |
| 22° | 0.721 | 0.704 |
| 32° | 0.716 | 0.728 |
| 36° | 0.746 | 0.737 |

The above proportionality is, however, not perfectly rigid. The exact formula is obtained, in case the work which the water attraction can perform is chosen as the starting-point. This is independent of whether the water is carried over as such, or as vapor; and thus we have the relation (for 18 kgs. water): —

$$2\,Tl \frac{p_w}{p_l} = \frac{1}{323} PV,$$

in which $p_w$ and $p_l$ are, respectively, the tension of the water and of the solution, $P$ the osmotic pressure in kgs. per qm., and $V$ the volume of 18 kgs. of water in cbm.

"This formula corresponds very accurately with Pfeffer's results, but it can be used for determining pressure only in case the tension $p_l$ is known; and thus Mitscherlich's question of water of crystallization is also solved, since it is evident that this water attraction corresponds to that of a solution of equal maximum tension. We have then the following: —

| Substance | Temperature | Pressure |
|---|---|---|
| $Na_2SO_4 . 10\ H_2O$ | 9° | 600 atmos. |
| $FeSO_4 . 7\ H_2O$ | 25° | 510 atmos. |
| $FeSO_4 . 7\ H_2O$ | 65° | 245 atmos. |
| $CuSO_4 . 5\ H_2O$ | 50° | 1100 atmos. |
| $CuSO_4 . 3\ H_2O$ | — | 1730 atmos. |

"This means that if $Na_2SO_4$ should be prevented from taking up its water by pressure, in a suitable manner, — say in Pfeffer's apparatus, — 600 atmospheres at 9° would be necessary and sufficient.

"We must now turn from Mitscherlich's question of affinity to dilute solutions; since where we are dealing with the union of water of crystallization, it is obvious that enormous concentrations obtain."

We see from the above paragraphs, the exact stages by which van't Hoff arrived at the study of dilute solutions from the standpoint of osmotic pressure. From the position of atoms in space, he was led to study reaction velocity, and from this the conditions of equilibrium. But closely connected with the problem of equilibrium was that of affinity. He took up, as an example of affinity, the attraction of salts for their water of crystallization, and sought to measure this more directly than had been done. This led him, through the suggestion of De Vries, directly to Pfeffer's osmotic investigations. Having dealt with concentrated solutions, he then turned to dilute; and we shall now learn the nature of the results which he obtained, by comparing the gas pressure of gases with the osmotic pressure of dilute solutions.

**Boyle's Law for Dilute Solutions.** — In 1887 van't Hoff published a paper in the first volume of the *Zeitschrift*

*für physikalische Chemie*, under the title, "The Rôle of Osmotic Pressure in the Analogy between Solutions and Gases."[1] The object of this communication, as its title implies, is to point out certain relations between the gas pressure of gases and the osmotic pressure of dilute solutions. To quote from the translation in Harper's Science Series: —

"The analogy between dilute solutions and gases acquires at once a more quantitative form, if we consider that in both cases the change in concentration exerts a similar influence on the pressure; and, indeed, the values in question are, in both cases, proportional to one another.

"This proportionality, which, for gases, is designated as Boyle's law, can be shown for osmotic pressure, experimentally from data already at hand, and also theoretically."

Van't Hoff then gives enough of Pfeffer's data to show experimentally, that there is proportionality between osmotic pressure and concentration.

"Let us first give the results of Pfeffer's determinations of osmotic pressure ($P$), in solutions of sugar, at the same temperature (13.2° to 16.1°) and different concentrations ($C$): —

| $C$ | $P$ | $\frac{P}{C}$ |
|---|---|---|
| 1% | 535 mm. | 535 |
| 2% | 1016 mm. | 508 |
| 2.74% | 1518 mm. | 554 |
| 4% | 2082 mm. | 521 |
| 6% | 3075 mm. | 513 |

"The nearly constant value of $\frac{P}{C}$ indicates that, in fact, a proportionality between pressure and concentration exists."[2]

[1] Ztschr. phys. Chem., 1, 481. Translated into English by H. C. Jones. Harper's Science Series, IV, p. 13.

[2] Harper's Science Series, IV, p. 16.

The work of De Vries[1] is then cited, as furnishing a second line of experimental evidence, of the applicability of Boyle's law to the osmotic pressure of dilute solution. De Vries compared the osmotic pressure of solutions of sugar, potassium nitrate, and potassium sulphate, with that of the contents of a plant cell, whose protoplasmic sac contracts when the cell is introduced into a solution which has stronger attraction for water. It was found that equal changes in concentration of solutions of sugar, potassium nitrate, and potassium sulphate, exert the same influence on the osmotic pressure. The experimental evidence was thus very strongly in favor of the law of Boyle for the osmotic pressure of solutions.

A theoretical demonstration of this law for solutions was also given by van't Hoff:[2]—

**Gay Lussac's Law for Dilute Solutions.** — Having found that the law of Boyle for gases applies to the osmotic pressure of solutions, one would naturally inquire whether other gas laws also apply to solutions. Thus, the attempt was made to apply to the osmotic pressure of solutions the law of Gay Lussac, which holds for the temperature coefficient of gas pressure. The law was tested both experimentally and theoretically on thermodynamic grounds.

For experimental demonstration, recourse was had again to the results of Pfeffer's investigations. This investigator found that the osmotic pressure always increased with rise in temperature. If from one of two experiments carried out with the same solution at different tempera-

[1] "Eine Methode zur Analyse der Turgorkraft," Pringsheim's Jahrb., 14.

[2] See Harper's Science Series, IV, 17.

tures we calculate the result of the other, on the assumption of Gay Lussac's law, and compare it with the value directly obtained, we have the following relations: —

1. Solution of cane-sugar.[1]

At 32° a pressure of 544 mm. was observed.

At 14.15° the calculated pressure is 512 mm., instead of 510 as found by experiment.

2. Solution of cane-sugar.

At 36° the pressure observed was 567 mm.

At 15.5° the calculated pressure is 529 mm., instead of 520.5 mm. as found experimentally.

3. Solution of sodium tartrate.

At 37.3° the pressure observed was 983 mm.

At 13.3° the calculated pressure is 907 mm., instead of 908 found by experiment.

There is evidently a close approximation, in the above results, between the observed and calculated values.

The law of Gay Lussac, as applied to the osmotic pressure of solutions, received further experimental support from the work of Donders and Hamburger.[2] They worked with animal cells (blood corpuscles) in a manner similar to De Vries. They found that solutions of potassium nitrate, sodium chloride, and sugar, which have the same osmotic pressure as the contents of the cells in question, at 0°, and therefore the same as one another, show exactly the same relation at 34°, *i.e.* all have the same osmotic pressure at this higher temperature.

This shows that the temperature coefficient of osmotic

[1] Harper's Science Series, IV, p. 19.

[2] Onderzoekingen gedaan in het physiologisth, Laboratorium der Utrechtsche Hoogeschool [3], 9, 26.

pressure for solutions of these three substances is the same; and, taken with Pfeffer's results, is strong evidence in favor of the law of Gay Lussac as applied to solutions.

**Experimental Evidence in Favor of both the Laws of Boyle and Gay Lussac for Solutions.** — It was observed by Soret,[1] that if a homogeneous solution is placed in a tube, and the top of the tube kept warmer than the bottom, the solution will not remain homogeneous, but will become more concentrated in the colder portion. This is exactly analogous to what would occur with a gas; the colder portion would become more concentrated. The experiments were made by Soret in vertical tubes, the upper portions of which were warmed to a constant temperature, and the lower portions cooled to a constant temperature. It was soon found, as would be expected, that the time required to establish equilibrium was much greater for solutions than for gases.

How does the "Principle of Soret" throw any light on the applicability of the laws of Boyle and Gay Lussac to solutions? A gas will always distribute itself in a space so that the gas pressure is the same at every point in the space. If one portion of the space is colder than another, the gas pressure of any given molecule in this portion will be less than in the warmer portion; therefore, more gas particles must collect in the colder portion, to give the same pressure as in the warmer portion of the tube.

Similarly, with solutions, the dissolved substance will distribute itself throughout the solvent, so that the osmotic pressure is the same at every point in the solution. If

[1] Archives des Sciences Phys. et Nat. [3], 2, 48; Ann. Chim. Phys. [5], 22, 293.

one part of the solution is colder than another, a dissolved particle will exert less osmotic pressure where the solution is colder. It will, therefore, require more particles in the colder region, to exert a given pressure, than in the warmer region. We can calculate the change in concentration of a gas with change in temperature, from the laws of Boyle and Gay Lussac. Similarly, if the laws of Boyle and Gay Lussac apply to the osmotic pressure of solutions, we can calculate the difference in concentrations between the colder and warmer parts of a solution, for a given difference in the temperature of these two regions. Then, the difference in the concentrations of the two parts can be determined experimentally, and the calculated results compared with the results of experiment.

This has been done for solutions of copper sulphate, and the following results are given by van't Hoff: —

1. Solution of copper sulphate.

The part cooled to 20° contained 17.332 per cent. The concentration calculated for 80°, is 14.3 per cent. That found experimentally was 14.03 per cent.

2. Solution of copper sulphate.

The part cooled to 20° contained 29.867 per cent. 24.8 per cent was calculated for 80°, while 23.871 per cent was found.

It should be observed, that the results found by experiment are slightly lower than those calculated on the basis of the laws of Boyle and Gay Lussac, yet the difference is only slight. It must, however, be stated in this connection, that it has been shown that the time required to establish equilibrium in a solution is much greater than was formerly supposed, and in the earlier experiments not enough time

was allowed for the final equilibrium to be reached. Consequently, the difference in concentration between the colder and the warmer portions of the tube, as found by experiment, was less than the calculated, since the latter was based on perfect equilibrium having been reached. More recent experiments, in which the tubes have been allowed to stand for several months, give results which agree very closely with the calculated, and thus the "Principle of Soret" is a strong experimental support, to the applicability of the laws of Boyle and Gay Lussac to the osmotic pressure of dilute solutions.

**Avogadro's Law for Dilute Solutions.** — It has been shown, thus far, that the osmotic pressure of solutions is proportional to the concentration, and, also, that the temperature coefficient of osmotic pressure is the same as that of gas pressure. In a word, gas pressure and osmotic pressure are analogous, both obeying the laws of Boyle and Gay Lussac.

The more important question, however, still remains: What is the relation between the actual osmotic pressure exerted by a dissolved particle, and the gas pressure of a gaseous particle, under the same conditions of temperature and concentration? Van't Hoff answered this question both experimentally and theoretically.

He found in Pfeffer's determinations of the osmotic pressure of cane-sugar, an experimental solution of this problem. The osmotic pressure of a sugar solution of known concentration was compared with the gas pressure of hydrogen gas, containing the same number of particles in a given space. A 1 per cent solution of sugar was used. Hydrogen of the same concentration would con-

tain $\frac{2}{342} \times 10$ grams per litre, *i.e.* 0.0581 gram per litre. Since hydrogen at 0° and atmospheric pressure weighs 0.08956 gram per litre, hydrogen under the above conditions would exert a pressure of $\frac{0.0581}{0.08956}$ atmosphere at 0°, or 0.649 atmosphere; and at $t°$ of $0.649(1 + 0.00367\,t)$ atmosphere.

Comparing this at different temperatures with Pfeffer's results, we have: —

| Temperature | Osmotic Pressure | Gas Pressure $0.649(1 + 0.00367\,t)$ |
|---|---|---|
| 6.8 | 0.664 | 0.665 |
| 13.7 | 0.691 | 0.681 |
| 14.2 | 0.671 | 0.682 |
| 15.5 | 0.684 | 0.686 |
| 22.0 | 0.721 | 0.701 |
| 32.0 | 0.716 | 0.725 |
| 36.0 | 0.746 | 0.735 |

These results suffice to bring out the relation, *that the osmotic pressure of a solution of sugar at a given temperature is exactly equal to the gas pressure of a gas, which contains the same number of molecules in a given volume as there are sugar molecules in the same volume of the solution.*

This relation has been found to hold for such a large number of substances, that we are led to the all-important generalization: *that the osmotic pressure of a dissolved particle is exactly equal to the gas pressure of a gaseous particle at the same temperature and concentration.*

The law of Avogadro, applied to gases, states that equal volumes of all gases, at the same temperature and pressure, contain the same number of ultimate particles.

The law of Avogadro, as applied to solutions, states that solutions which, at the same temperature, have the same osmotic pressure, contain in a given volume the same number of dissolved particles.

Van't Hoff has shown that the law of Avogadro, as applied to solutions, is confirmed also by the lowering of the vapor-tension, and of the freezing-point of the solvent, produced by the dissolved substance.

He has also given a thermodynamic demonstration of the law.[1]

**General Expression of the Laws of Boyle, Gay Lussac, and Avogadro, for Solutions and Gases.** — Having shown that the three laws of gas pressure apply to the osmotic pressure of solutions, van't Hoff attempted to furnish a general expression for these three laws. "The well-known formula, which expresses for gases the two laws of Boyle and Gay Lussac:—

$$PV = RT,$$

is now, where the laws referred to are also applicable to liquids, valid also for solutions, if we are dealing with the osmotic pressure. This holds even with the same limitation, which is also to be considered with gases, that the dilution shall be sufficiently great to allow one to disregard the reciprocal action of, and the space taken by, the dissolved particles.

"If we wish to include in the above expression also the third, the law of Avogadro, this can be done in an exceedingly simple manner, following the suggestion of Horstmann,[2] considering always kilogram molecules of the

[1] See Harper's Science Series, IV, 22. [2] Ber. d. chem. Gesell., 14, 1243.

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substance in question; thus, 2 k. hydrogen, 44 k. carbon dioxide, etc. Then $R$ in the above equation has the same value for all gases, since, at the same temperature and pressure, the quantities mentioned occupy also the same volume. If this value is calculated, and the volume taken in $Mr^3$, the pressure in $K°$ per $Mr^2$, and if, for example, hydrogen at 0° and atmospheric pressure is chosen: —

$$P = 10333,\ V = \frac{2}{0.08956},\ T = 273,\ R = 845.05.$$

The combined expression of the laws of Boyle, Gay Lussac, and Avogadro is then: —

$$PV = 845\ T,$$

and, in this form, it refers not only to gases, but to all solutions, $P$ being then always taken as osmotic pressure."[1] The conclusion from what has thus far been given of van't Hoff's paper is that the three laws of gas pressure apply directly to the osmotic pressure of solutions, and this is perfectly general for solutions such as we have been considering. But there are many exceptions, and these are of even more interest than the cases which conform to the laws of gas pressure.

**Exceptions to the General Applicability of the Gas Laws to Osmotic Pressure.** — While the osmotic pressures of solutions of compounds like cane-sugar conform to the gas laws, the osmotic pressures of large classes of chemical substances do not conform to these laws. *The exceptions include all the acids, all the bases, and all the salts.* If we will consider the number of compounds contained in

[1] Harper's Science Series, IV, 24.

these three classes, it is a question whether the exceptions will not outnumber the cases which conform to rule.

*All of these compounds give an osmotic pressure, which is greater than would be expected from the gas laws.*

The expression $PV = RT$ no longer applies to the osmotic pressure of these substances, and, therefore, a coefficient was introduced by van't Hoff; when the expression became: —

$$PV = iRT.$$

This coefficient, which for acids, bases, and salts is always greater than unity, has come to be known as the "van't Hoff *i*." What was the real physical or chemical significance of these exceptions? Why does a large class of compounds show an osmotic pressure which conforms to the gas laws, and yet a very large class give an osmotic pressure which is always too great?

Van't Hoff saw clearly the discrepancy which existed here, as will be seen from his own words: "If we are still considering 'ideal solutions,' a class of phenomena must be dealt with which, from the now clearly demonstrated analogy between solutions and gases, are to be classed with the earlier so-called deviations from Avogadro's law. As the pressure of the vapor of ammonium chloride, for example, was too great in terms of this law, so, also, in a large number of cases, the osmotic pressure is abnormally large, and in the first case, as was afterwards shown, there is a breaking down into hydrochloric acid and ammonia, so, also, with solutions, we would naturally conjecture that, in such cases, a similar decomposition had taken place. Yet it must be conceded that anomalies of this kind, existing

in solutions, are much more numerous, and appear with substances which it is difficult to assume break down in the usual way. Examples in aqueous solutions are most of the salts, the strong acids, and the strong bases. . . . It may then have appeared daring to give Avogadro's law for solutions such a prominent place, and I should not have done so, had not Arrhenius pointed out to me, by letter, the probability that salts and analogous substances, when in solution, break down into ions." [1]

The last sentence gives us the connecting link between the generalization reached by van't Hoff, and the discovery of the theory of electrolytic dissociation. The latter we owe to the Swedish physicist, Arrhenius, to whose work we will now turn.

### ON THE DISSOCIATION OF SUBSTANCES DISSOLVED IN WATER BY SVANTE ARRHENIUS

A paper,[2] under the above title, appeared in the same volume of the *Zeitschrift für physikalische Chemie*, as the paper by van't Hoff which we have just considered. Arrhenius was impressed by the generalizations reached by van't Hoff, and especially by the large number of exceptions. This will be seen best by quoting the words with which Arrhenius began his paper.

"In a paper submitted to the Swedish Academy of Sciences, on the 14th of October, 1895, van't Hoff proved experimentally, as well as theoretically, the following unusually significant generalization of Avogadro's law: —

[1] Harper's Science Series, IV, 34.

[2] Ztschr. phys. Chem., I, 631 (1887). Translated into English by H. C. Jones. Harper's Science Series, IV, 47.

"The pressure which a gas exerts at a given temperature, if a definite number of molecules is contained in a definite volume, is equal to the osmotic pressure which is produced by most substances under the same conditions, if they are dissolved in any given liquid." [1]

"Van't Hoff has proved this law in a manner which scarcely leaves any doubt as to its absolute correctness. But a difficulty which still remains to be overcome, is that the law in question holds only for 'most substances,' a very considerable number of the aqueous solutions investigated furnishing exceptions; and in the sense that they exert a much greater osmotic pressure than would be required from the law referred to."

The above are the words with which Arrhenius stated the problem; we will now follow the line of thought which led him to its solution.

"If a gas shows such a deviation from the law of Avogadro, it is explained by assuming that the gas is in a state of dissociation. The conduct of chlorine, bromine, and iodine, at higher temperatures, is a very well-known example. We regard these substances, under such conditions, as broken down into simple atoms.

"The same expedient may, of course, be made use of to explain the exceptions to van't Hoff's law; but it has not been put forward up to the present, probably on account of the newness of the subject, the many exceptions known, and the vigorous objections which would be raised from the chemical side to such an explanation. The purpose of the following lines is to show that such an assumption,

[1] Van't Hoff, Une propriété générale de la matière diluée, p. 43. Sv. Vet-ak-s Handlingar, 21, Nr. 17, 1886.

of the dissociation of certain substances dissolved in water, is strongly supported by the conclusions drawn from the electrical properties of the same substances, and that, also, the objections to it from the chemical side are diminished on more careful examination." [1]

Arrhenius then offers his explanation of the exceptions to van't Hoff's generalization. As we shall see, he goes back to the theory put forward by Clausius to account for electrolysis, and which has already been considered, in connection with the development of electrochemistry (p. 48).

"In order to explain the electrical phenomena, we must assume with Clausius,[2] that some of the molecules of an electrolyte are dissociated into their ions, which move independent of one another. But since the 'osmotic pressure' which a substance dissolved in a liquid exerts against the walls of the confining vessel must be regarded, in accordance with the modern kinetic view, as produced by the impacts of the smallest parts of this substance, as they move against the walls of the vessel, we must therefore assume, in accordance with this view, that a molecule dissociated in the manner given above, exercises as great a pressure against the walls of the vessel as its ions would do in the free condition. If, then, we could calculate what fraction of the molecules of an electrolyte is dissociated into ions, we should be able to calculate the osmotic pressure from van't Hoff's law." [3]

We see from the above, that the simple qualitative suggestion, that some molecules are broken down into parts or

[1] Harper's Science Series, IV, 48.
[2] Pogg. Ann., 101, 347; Wied. Elektr., 2, 941.
[3] Harper's Science Series, IV, 48.

ions, is not new with Arrhenius. This theory, as already stated, had been advanced some thirty years before by Clausius. The new feature, which was introduced by Arrhenius, was to point out a method of determining just what per cent of the molecules are broken down into ions. The merely qualitative suggestion of Clausius was thus converted into a definite theory, which could be tested experimentally. The method of calculating the amount of dissociation into ions, as worked out by Arrhenius, will now be given in his own words.

"In a former communication, 'On the Electrical Conductivity of Electrolytes,' I have designated those molecules, whose ions are independent of one another in their movements, as active; the remaining molecules, whose ions are firmly combined with one another, as inactive. I have also maintained it as probable, that in extreme dilution, all the inactive molecules of an electrolyte are transformed into active.[1] This assumption I will make the basis of the calculations now to be carried out. I have designated the relation between the number of active molecules, and the sum of the active and inactive molecules, as the activity coefficient.[2] The activity coefficient of an electrolyte at infinite dilution is therefore taken as *unity*. For smaller dilution it is less than *one*, and from the principles established in my work already cited, it can be regarded as equal to the ratio of the actual molecular conductivity of the solution, to the maximum limiting value which the molecular conductivity of the same solution approaches with

[1] *Bihang der Stockholmer Akademie*, 8, Nr. 13 and 14, 2 Tl., pp. 5 and 13; 1 Tl., p. 6.

[2] *Loc. cit.*, 2 Tl., p. 5.

increasing dilution. This obtains for solutions which are not too concentrated (*i.e.* for solutions in which disturbing conditions, such as internal friction, etc., can be disregarded). If this activity coefficient ($\alpha$) is known, we can calculate, as follows, the values of the coefficient $i$, tabulated by van't Hoff: $i$ is the relation between the osmotic pressure actually exerted by a substance, and the osmotic pressure which it would exert, if it consisted only of inactive (undissociated) molecules. $i$ is evidently equal to the sum of the number of inactive molecules, plus the number of ions, divided by the sum of the inactive and active molecules. If, then, $m$ represents the number of inactive, and $n$ the number of active, molecules, and $k$ the number of ions into which every active molecule dissociates (*e.g.*, $k = 2$ for KCl, *i.e.* K and Cl; $k = 3$ for $BaCl_2$ and $K_2SO_4$, *i.e.* Ba, Cl, Cl, and K, K, $SO_4$), then we have: —

$$i = \frac{m + kn}{m + n}.$$

"But since the activity coefficient ($\alpha$) can, evidently, be written $\frac{n}{m+n}$: —

$$i = 1 + (k - 1)\alpha.''$$ [1]

Arrhenius thus shows how it is possible to calculate the value of the van't Hoff coefficient $i$, knowing the activity coefficient ($\alpha$), which can be determined directly from the conductivity of the solution.

He then shows how the value of $i$ can be calculated also from the lowering of the freezing-point of water produced by the dissolved substance.

[1] Harper's Science Series, IV, 48.

"On the other hand, $i$ can be calculated as follows, from the results of Raoult's experiments on the freezing-point of solutions, making use of the principles stated by van't Hoff. The lowering ($t$) of the freezing-point of water (in degrees Celsius), produced by dissolving a gram-molecule of the given substance in one litre of water, is divided by 18.5:—

$$i = \frac{t}{18.5}."^{1}$$

Arrhenius then compared the values of $i$, calculated from the conductivity of solution, with the values calculated from the freezing-point lowerings, to see whether the two series would agree with one another. He made the comparison for a large number of bases, acids, and salts, and also for a number of organic compounds, where the value of $i$ is unity. A few examples from each class of compounds will be given, since it is a matter of the very greatest importance to determine whether the two values of $i$ agree. If they do, the theory just advanced is made quite probable. If they do not, it is almost a conclusive argument against the correctness of the theory.

BASES

| SUBSTANCE | | $i=\frac{t}{18.5}$ | $i=1+(k-1)\alpha$ |
|---|---|---|---|
| Barium hydroxide, | $Ba(OH)_2$ | 2.69 | 2.67 |
| Strontium hydroxide, | $Sr(OH)_2$ | 2.61 | 2.72 |
| Calcium hydroxide, | $Ca(OH)_2$ | 2.59 | 2.59 |
| Sodium hydroxide, | $NaOH$ | 1.96 | 1.88 |
| Potassium hydroxide, | $KOH$ | 1.91 | 1.93 |
| Ammonia, | $NH_3$ | 1.03 | 1.01 |
| Methylamine, | $CH_3NH_2$ | 1.00 | 1.03 |
| Trimethylamine, | $(CH_3)_3N$ | 1.09 | 1.03 |
| Ethylamine, | $C_2H_5NH_2$ | 1.00 | 1.04 |
| Aniline, | $C_6H_5NH_2$ | 0.83 | 1.00 |

[1] Harper's Science Series, IV. 49.

### Acids

| | | | |
|---|---|---|---|
| Hydrochloric acid, | $HCl$ | 1.98 | 1.90 |
| Hydrobromic acid, | $HBr$ | 2.03 | 1.94 |
| Nitric acid, | $HNO_3$ | 1.94 | 1.92 |
| Chloric acid, | $HClO_3$ | 1.97 | 1.91 |
| Sulphuric acid, | $H_2SO_4$ | 2.06 | 2.19 |
| Sulphurous acid, | $H_2SO_3$ | 1.03 | 1.28 |
| Formic acid, | $HCOOH$ | 1.04 | 1.03 |
| Acetic acid, | $CH_3COOH$ | 1.03 | 1.01 |
| Tartaric acid, | $C_4H_6O_6$ | 1.05 | 1.11 |
| Malic acid, | $C_4H_6O_5$ | 1.08 | 1.07 |
| Lactic acid, | $C_3H_6O_3$ | 1.01 | 1.03 |

### Salts

| Substance | | $i=\frac{t}{18.5}$ | $i=1+(k-1)\alpha$ |
|---|---|---|---|
| Potassium chloride, | $KCl$ | 1.82 | 1.86 |
| Sodium chloride, | $NaCl$ | 1.90 | 1.82 |
| Ammonium chloride, | $NH_4Cl$ | 1.88 | 1.84 |
| Potassium cyanide, | $KCN$ | 1.74 | 1.88 |
| Potassium nitrate, | $KNO_3$ | 1.67 | 1.81 |
| Potassium acetate, | $CH_3COOK$ | 1.86 | 1.83 |
| Silver nitrate, | $AgNO_3$ | 1.60 | 1.86 |
| Potassium sulphate, | $K_2SO_4$ | 2.11 | 2.33 |
| Ammonium sulphate, | $(NH_4)_2SO_4$ | 2.00 | 2.17 |
| Barium chloride, | $BaCl_2$ | 2.63 | 2.54 |
| Strontium chloride, | $SrCl_2$ | 2.76 | 2.50 |
| Calcium chloride, | $CaCl_2$ | 2.70 | 2.50 |
| Barium nitrate, | $Ba(NO_3)_2$ | 2.19 | 2.13 |
| Strontium nitrate, | $Sr(NO_3)_2$ | 2.23 | 2.23 |
| Calcium nitrate, | $Ca(NO_3)_2$ | 2.02 | 2.33 |
| Mercuric chloride, | $HgCl_2$ | 1.11 | 1.05 |
| Cadmium nitrate, | $Cd(NO_3)_2$ | 2.32 | 2.46 |

ORGANIC COMPOUNDS

| | | | |
|---|---|---|---|
| Methyl alcohol, | $CH_4O$ | 0.94 | 1.00 |
| Ethyl alcohol, | $C_2H_6O$ | 0.94 | 1.00 |
| Butyl alcohol, | $C_4H_{10}O$ | 0.93 | 1.00 |
| Mannite, | $C_6H_{14}O_6$ | 0.97 | 1.00 |
| Invert sugar, | $C_6H_{12}O_6$ | 1.04 | 1.00 |
| Cane-sugar, | $C_{12}H_{22}O_{11}$ | 1.00 | 1.00 |
| Phenol, | $C_6H_6O$ | 0.84 | 1.00 |
| Acetone, | $C_3H_6O$ | 0.92 | 1.00 |

That there is a general agreement between the two values of $i$, in the above tables, is evident. That there are some discrepancies, is just what would be expected, from the experimental errors contained in both the freezing-point and the conductivity methods. It must be further borne in mind, that the freezing-point method was very imperfectly developed when the above determinations were made.

Another cause of these discrepancies was pointed out by Arrhenius, as follows: —

"There is one condition which interferes, possibly very seriously, with directly comparing the figures in the last two columns; namely, that the values really hold for different temperatures. All the figures in next to the last column hold, indeed, for temperatures only a very little below 0° C., since they were obtained from experiments on inconsiderable lowerings of the freezing-point of water. On the other hand, the figures of the last column for acids and bases (Ostwald's experiments) hold at 25°, the others at 18°. The figures of the last column for non-conductors hold, of course, also at 0° C, since these substances, at this

temperature, do not consist, to any appreciable extent, of dissociated (active) molecules." [1]

Arrhenius then refers to the general agreement between the two sets of values in the following terms: —

"An especially marked parallelism appears, beyond doubt, on comparing the figures in the last two columns. This shows *a posteriori*, that in all probability the assumptions on which I have based the calculation of these figures are, in the main, correct. These assumptions were: —

"1. That van't Hoff's law holds not only for *most*, but for *all*, *substances*, even for those which have hitherto been regarded as exceptions (electrolytes in aqueous solution).

"2. That every electrolyte (in aqueous solution) consists partly of active, (in chemical and electrical relation) and partly of inactive, molecules, the latter passing into active molecules on increasing the dilution, so that in infinitely dilute solutions only active molecules exist. Arrhenius then calls attention to the difference between the kind of dissociation indicated here, and that shown when a vapor-like ammonium chloride dissociates by heat.

"Although the dissolved substance exercises an osmotic pressure against the wall of the vessel, just as if it were partly dissociated into its ions, yet the dissociation with which we are here dealing is not exactly the same as that which exists when, *e.g.*, an ammonium salt is decomposed at a higher temperature. The products of dissociation in the first case (the ions) are charged with very large quantities of electricity, of opposite kind, whence certain conditions appear (the incompressibility of electricity), from which it follows that the ions cannot be separated from

[1] Harper's Science Series, IV, 54.

one another to any great extent without a large expenditure of energy. On the contrary, in ordinary dissociation, where no such conditions exist, the products of dissociation can, in general, be separated from one another." [1]

Although Arrhenius pointed out, so clearly, the characteristic feature of the dissociation which he believed electrolytes to undergo in the presence of water, namely, that the products of dissociation were charged, the one always positively, the other always negatively, yet this has often been overlooked.

**Summary.** — In concluding this chapter, we will briefly recall the steps which led to the theory of electrolytic dissociation. The stages by which van't Hoff passed from the study of the position of atoms in space to Pfeffer's work on osmotic pressure have been followed in detail. Van't Hoff showed, from Pfeffer's results, and also theoretically, that the laws of Boyle, Gay Lussac, and Avogadro, for gas pressure, apply to the osmotic pressure of solutions.

But these apply only to solutions of non-electrolytes, *i.e.* substances which, when in the presence of water, do not conduct the current. All electrolytes, *i.e.* the acids, bases, and salts, are exceptions, showing greater osmotic pressure than would accord with the laws of gas pressure. To what was this discrepancy due? Since osmotic pressure is proportional to the number of parts present, too great osmotic pressure means more parts present than would be expected.

In order that we might have more parts present than the molecules, it is necessary that the molecules should undergo decomposition. How is it possible to think of

[1] Harper's Science Series, IV, 54.

stable molecules, such as hydrochloric acid, potassium hydroxide, potassium chloride, suffering decomposition? Arrhenius furnished the answer. He had resort to the old theory proposed by Clausius, to account for electrolysis, that in the presence of water the molecules are broken down into ions. Arrhenius pointed out two ways of calculating the amount of this dissociation, the one based on conductivity, the other on freezing-point lowering, and showed that the results from the two methods agreed.

All of the compounds which give abnormally great osmotic pressure, and are therefore dissociated into ions, conduct the current when in solution in water, and are therefore electrolytes. This kind of dissociation has come to be known as *electrolytic*, and the theory advanced by Arrhenius as the *Theory of Electrolytic Dissociation*.

It is one thing to propose a theory, and another to propose a theory which is true. In the next chapter we will consider some of the lines of evidence bearing upon the theory of electrolytic dissociation.

# CHAPTER III

## EVIDENCE BEARING UPON THE THEORY OF ELECTROLYTIC DISSOCIATION

### THE PHYSICAL PROPERTIES OF COMPLETELY DISSOCIATED SOLUTIONS SHOULD BE ADDITIVE

A theory in science must, first of all, be capable of experimental test. If it cannot be shown to be either true or false, it is of little value as a scientific generalization.

Arrhenius pointed out in his first paper, that evidence bearing upon his theory could be obtained from a study of the physical properties of solutions, whose dissociation, in terms of the theory, was supposed to be complete. "If a salt (in aqueous solution) is completely broken down into its ions, most of the properties of this salt can, of course, be expressed as the sum of the properties of the ions; since the ions are independent of one another in most cases, and since every ion has therefore a characteristic property, independent of the nature of the opposite ion with which it occurs."

He also observed that we rarely have to do with completely dissociated solutions. Those of the salts, strong acids, and strong bases, are dissociated only from 80 to 90 per cent, at ordinary dilutions, and the additive nature of the properties of even such solutions would be only approximate. Another class of substances, such as mercuric

chloride, cadmium iodide, and all of the weak acids and bases, organic and inorganic, are comparatively little dissociated by water at moderate dilutions, and the physical properties of solutions of these substances are not those of the ions alone, but of both ions and molecules.

The point, in a word, is this: The physical properties of completely dissociated solutions must be a function of the physical properties of the ions, as there are no molecules present. Since each ion has its own specific properties, independent of the nature of the other ion with which it is associated, the physical properties of completely dissociated solutions must be the *sum* of the physical properties of the ions in those solutions. If the solutions are not completely dissociated, their properties are those both of the ions and of the molecules.

We must now study the physical properties of completely dissociated solutions, and see what relations exist between these and the physical properties of the ions which they contain. We will take solutions of salts.

**Specific Gravity of Salt Solutions.** — If a salt is added to water, the volume of the solution is different from that of the pure solvent, and also from the sum of the volumes of the liquid and the solid. If the resulting solution is very dilute, the salt is completely dissociated into its ions. Nernst[1] has shown, from the results of J. Traube,[2] that the change in volume under such conditions is an additive property of the ions. Given a solution containing a gram-molecular weight of a salt whose molecular weight is $M$, in $m$ grams of water. Let the specific gravity of

[1] Theoretische Chemie, p. 317. [2] Ztschr. anorg. Chem., 3, 1.

the solution be $S$, the specific gravity of water $s$. The change in volume $\Delta v$, on dissolving the salt, will be: —

$$\Delta v = \frac{M+m}{S} - \frac{m}{s}.$$

The following results are given: —

| | |
|---|---|
| KCl = 26.7 | NaCl = 17.7 |
| KBr = 35.1 | NaBr = 26.7 |
| KI = 45.4 | NaI = 36.1 |

| | |
|---|---|
| KBr − KCl = 8.4 | KI − KBr = 10.3 |
| NaBr − NaCl = 9.0 | NaI − NaBr = 9.4 |
| KI − KCl = 18.7 | KCl − NaCl = 9.0 |
| NaI − NaCl = 18.4 | KBr − NaBr = 8.4 |
| | KI − NaI = 9.3 |

These results show the additive nature of the specific gravity of salt solutions. The difference between the chlorine and the bromine ions is about 8.7; between chlorine and iodine 18.5; between bromine and iodine 9.8; while between potassium and sodium it is about 9.0.

The additive nature of the specific gravity of salt solutions had, indeed, been pointed out much earlier by Valson.[1] He had shown exactly what is brought out above: Given salt solutions of comparable concentration, *i.e.* containing say a gram-molecule of the salt per litre, the difference between the specific gravities of solutions containing two metals combined with the same acid is constant, whatever the nature of the acid. Similarly, the difference between the specific gravities of two salts of the same acid with any metal is constant, regardless of

[1] Compt. rend., 73, 441 (1874).

the nature of the metal. The specific gravity of a salt solution is, then, obtained by adding to a constant number two values, — the one for the acid, the other for the metal. These values Valson termed "moduli"; and he worked out their values for a large number of elements.

Valson[1] concluded from his work, that the molecules of salts must be completely broken down in solution. But the evidence in favor of such a view was not strong enough at that time to bring it into favor.

**Change of Volume in Neutralization.** — The change of volume produced by neutralizing acids with bases has been extensively studied by Ostwald.[2] The solutions contained a gram-equivalent of the acid or base, in a kilogram, and were, therefore, not completely dissociated; so that, if the change in volume was additive, it would be shown only approximately by such solutions.

Ostwald[3] worked with nineteen acids, including the strongest mineral acids, and some of the more strongly dissociated organic acids. He neutralized these with the three bases, potassium, sodium, and ammonium. A few of his results are given, the change in volume being expressed in cubic centimetres. The differences in the horizontal lines are the differences between potassium, sodium, and ammonium, in combination with the same acid. The differences in the vertical columns are the differences between the different acids in combination with the same bases, obtained by subtracting the value for the acid from the value for nitric acid.

[1] Compt. rend., 73, 441; 74, 103; 75, 1033. [2] Journ. prakt. Chem. [2], 18, 353.
[3] Lehrb. d. allg. Chem. I, p. 788.

| | Potassium Hydroxide | Sodium Hydroxide | Ammonium Hydroxide |
|---|---|---|---|
| Nitric acid, | 20.05 (0.28) | 19.77 (26.21) | — 6.44 (26.49) |
| | (0.53) | (0.53) | (0.13) |
| Hydrochloric acid, | 19.52 (0.28) | 19.24 (25.81) | — 6.57 (26.09) |
| | (7.69) | (7.61) | (7.15) |
| Formic acid, | 12.36 (0.20) | 12.16 (25.75) | — 13.59 (25.95) |
| | (10.53) | (10.49) | (9.82) |
| Acetic acid, | 9.52 (0.24) | 9.28 (25.54) | — 16.26 (25.78) |
| | (8.15) | (8.29) | (7.91) |
| Sulphuric acid, | 11.90 (0.42) | 11.48 (25.83) | — 14.35 (26.25) |
| | (11.82) | (11.84) | (11.19) |
| Succinic acid, | 8.23 (0.30) | 7.93 (25.56) | — 17.63 (25.86) |

If we take the perpendicular rows in parentheses, we find very nearly a constant difference for the strong acids and bases. Similarly, if we take the horizontal rows in parentheses, we find very nearly a constant difference. This means that the difference of change in volume, produced by neutralizing two different bases by a given acid, is a constant, independent of the nature of the acid; and, similarly, the difference of the change in volume on neutralizing two different acids by a given base, is independent of the nature of the base.

The change in volume, when acids and bases neutralize each other, like the specific gravity of salt solutions, is, then, an additive property, depending both upon the nature of the acid and of the base; and we could work out here, as Valson has done in the case of specific gravities, the numerical values of the constants for each constituent.

**Specific Refractive Power of Salt Solutions.** — Gladstone calculated the refraction equivalents $R$, of a number of elements, from the formula: —

$$R = P\frac{n-1}{d},$$

in which $P$ is the weight of the substance, $n$ the index of refraction, and $d$ the density. He also showed that the refraction coefficients of salts were the sum of the refraction equivalents of the elements.

That this is true is seen from the following table of results, taken by Arrhenius[1] from the Lehrbuch of Ostwald.[2] Only a few examples are given here.

| | Hydrogen | | Potassium | | Sodium |
|---|---|---|---|---|---|
| Chloride, | 14.44 | (4.00) | 18.44 | (3.3) | 15.11 |
| | (6.2) | | (6.9) | | (6.6) |
| Bromide, | 20.63 | (4.7) | 25.34 | (3.6) | 21.70 |
| | (3.4) | | (3.5) | | (3.0) |
| Nitrate, | 17.24 | (4.6) | 21.80 | (3.1) | 18.66 |
| | (4.0) | | (5.8) | | (5.4) |
| Acetate, | 21.20 | (6.4) | 27.65 | (3.6) | 24.05 |
| | (24.0) | | (30.0) | | (26.4) |
| Tartrate, | 45.18 | (12.4) | 57.60 | (7.2) | 50.39 |

The differences, both horizontally and vertically, are as constant as could be expected, except for the two organic acids which, at the dilutions employed, are only slightly dissociated. This means that the different effect of potassium and hydrogen, on the refraction equivalent, is constant, whatever the acid with which they are combined, and the same holds for potassium and sodium. Also, that chlorine, bromine, etc., have a constant effect on the refractive power, whether they are combined with hydrogen, potassium, or sodium. In a word, the refractive power of salt

[1] Ztschr. phys. Chem., 1, 645. Harper's Science Series, IV, 62.
[2] Lehrb. d. allg. Chem., II, p. 446.

solutions is distinctively an additive property of the constituents.

**Rotatory Power of Salt Solutions.** — The power possessed by solutions of some salts to rotate the plane of polarization of light, must be a property of the optically active constituent of the salt, or, if both constituents are optically active, it must be the sum of the activities of the two. Oudemans[1] has shown that optically active bases, such as the monacid alkaloids, produce the same rotation, regardless of the nature of the optically inactive acid with which they are combined. And optically active acids rotate the plane of polarization, independent of the nature of the inactive base combined with them. This is very well shown by the work of Hartmann,[2] on the salts of camphoric acid.

| $Li_2$ | Mg | $(NH_4)_2$ | Ca | $Na_2$ | $K_2$ | Ba |
|---|---|---|---|---|---|---|
| 37.5 | 39.5 | 38.4 | 39.1 | 36.0 | 36.1 | 36.5 |

The rotatory power of salts of this acid is practically constant, independent of the nature of the base combined with it.

**The Color of Salt Solutions.** — The absorption which light undergoes, in passing through a solution of a completely dissociated substance must, in terms of our theory, be the sum of the absorption of the cation, plus that of the anion. If one of the ions is colorless, the absorption must be entirely that of the other ion.

That this is qualitatively true is a matter of common experience. We utilize the color of solutions to determine the nature of their constituents. Thus, cupric salts in dilute aqueous solutions are blue, or bluish green, regardless

[1] Beibl., 9, 635. [2] Ber. d. chem. Gesell. (1888), 221.

of the chemical nature of the anion with which the copper is combined, provided that it is colorless. Likewise, the chromates are yellow, and the salts of nickel green.

A method for determining, quantitatively, whether the absorption of light is additive, is to prepare a number of salts of an acid whose anion is colored, the cation being always colorless. Then determine whether all of the salts have the same absorption spectrum. The metallic salts of permanganic acid are particularly well adapted to this purpose, and they have been thoroughly studied by Ostwald[1] in this connection. These salts show five absorption bands in the yellow and green, and four of these have been measured by Ostwald for thirteen salts of permanganic acid. The results are so striking, that they are given in the following table: —

| | Permanganates. | Absorption Bands. | | |
|---|---|---|---|---|
| | I | II | III | IV |
| Hydrogen, | 2601 ± 0.5 | 2698 ± 0.8 | 2804 ± 0.7 | 2913 ± 1.7 |
| Potassium, | 2600 ± 1.3 | 2697 ± 0.1 | 2803 ± 0.9 | 2913 ± 1.1 |
| Sodium, | 2602 ± 1.2 | 2698 ± 0.8 | 2803 ± 0.7 | 2913 ± 0.8 |
| Ammonium, | 2601 ± 1.3 | 2698 ± 1.4 | 2802 ± 0.1 | 2913 ± 0.1 |
| Lithium, | 2602 ± 0.2 | 2700 ± 0.2 | 2804 ± 0.8 | 2914 ± 1.7 |
| Barium, | 2600 ± 0.9 | 2699 ± 0.8 | 2804 ± 0.6 | 2914 ± 1.3 |
| Magnesium, | 2602 ± 0.8 | 2700 ± 0.6 | 2802 ± 0.7 | 2912 ± 1.8 |
| Aluminium, | 2603 ± 0.4 | 2699 ± 0.9 | 2804 ± 0.9 | 2914 ± 0.7 |
| Zinc, | 2602 ± 0.5 | 2699 ± 0.7 | 2802 ± 1.2 | 2912 ± 1.1 |
| Cobalt, | 2601 ± 0.2 | 2698 ± 0.1 | 2803 ± 0.9 | 2912 ± 1.7 |
| Nickel, | 2603 ± 0.5 | 2700 ± 0.7 | 2804 ± 0.7 | 2913 ± 1.8 |
| Cadmium, | 2600 ± 0.1 | 2700 ± 0.2 | 2803 ± 0.8 | 2913 ± 1.4 |
| Copper, | 2602 ± 1.2 | 2699 ± 0.1 | 2803 ± 0.9 | 2913 ± 0.8 |

[1] Ztschr. phys. Chem., 9, 584.

From these results, Ostwald concluded that the absorption spectra of the thirteen permanganates are just the same.

A large number of other compounds were investigated,[1] including ten salts of fluorescein, ten of eosin yellow, ten of eosin blue, ten of iodoeosin, ten of dinitrofluorescein, rosolic acid, and a number of other substances. Also a large number of cases were studied, where a colored cation was combined with a number of colorless anions. Thus, the salts of pararosaniline with twenty colorless acids, and an equal number of the salts of aniline violet, were investigated.

Ostwald studied, in all, about three hundred cases, to determine whether the color of a solution with one colored ion is effected at all by the presence of the colorless ion. He concluded that salts with one and the same colored ion, in dilute solution, always show exactly the same absorption spectra.

The elaborate investigation just considered shows conclusively, that the color of salt solutions is exactly the color of the colored ion, and from this it follows, that if both ions were colored, the color of the solution would be the sum of the colors of the two ions. The color of salt solutions is, therefore, an additive property.

The use of *indicators* in quantitative analysis is based upon this fact. That a substance may be used as an indicator for acids and bases, it is necessary that one of the ions should have a different color from the molecule. Take the case of phenolphthalein. Its alcoholic solution is nearly colorless, and since it does not conduct the

[1] *Loc. cit.*

current, it is undissociated. The molecules of phenolphthaleïn are, therefore, colorless. If we add an alkali, say sodium hydroxide, to phenolphthaleïn, the sodium salt is formed; but this dissociates at once into the cation sodium, and the complex organic anion, which is deeply colored. The characteristic color of phenolphthaleïn, acting as an indicator for an alkali, is, then, always the color of the complex anion. If to the colored solution a little acid is added, the original phenolphthaleïn is formed, and is colorless.

Take, on the other hand, the basic indicator, cyanine; the molecules of the free base are blue. It is a weak base, and, therefore, but little dissociated. Add acid; the salt is formed, which at once dissociates. The complex organic anion is colorless, and, hence, on adding acid, the color due to the molecules of the free base disappears. This is exactly the opposite of the case first considered.

Finally, take methyl orange, where the molecules are yellow. Add an acid, the salt is formed, and this breaks down at once into ions. The color of the complex organic anion is, in this case, red. The addition of acid, therefore, brings out the characteristic color of this indicator.

A number of other cases might be taken up, where the molecule is either colorless, or has a different color from one of its ions, but the cases considered are typical, and suffice to make the point clear.

**A Demonstration of the Dissociating Action of Water.** — Jones and Allen[1] have worked out a color demonstration of the dissociating action of water, which is based upon the principle of indicators just considered. If, to an

[1] Amer. Chem. Journ., 18, 377.

alcoholic solution of phenolphthalein, a few drops of aqueous ammonia are added, there is no sign of the red color of the indicator. If water is now added to the alcoholic solution, the red color appears. When potassium or sodium hydroxide is substituted for ammonia, the red color appears at once, without the addition of water. There is, thus, a marked difference between potassium and sodium hydroxide and ammonium hydroxide.

It would be difficult to interpret these facts without the aid of the theory of electrolytic dissociation. In the light of this theory they are perfectly intelligible.

When a few drops of aqueous ammonia are added to several cubic centimetres of alcohol, little or no dissociation of the ammonium hydroxide is effected. The addition of water dissociates the base, the degree of dissociation depending upon the amount of water present with respect to alcohol. The presence of the ions $\overset{+}{N}H_4$ and $\overset{-}{O}H$ would cause the phenolphthalein to dissociate. The complex anion gives its characteristic color to the solution in which it is present. The hydrogen and hydroxyl ions would then combine and form water.

It is possible that the actual course of the reaction is somewhat different from that just described. It may be that the ammonium group first combines with the phenolphthalein in the alcoholic solution. The addition of water would then dissociate this compound, giving the colored anion referred to above.

The dissociation theory furnishes this explanation. It remains to determine whether the explanation is true.

If it is, then a solution, formed by adding a little aqueous ammonia to a considerable volume of alcohol, should show

little or no dissociation, and the amount of the dissociation should increase with the addition of water. Solutions of potassium or sodium hydroxide, in mixtures of alcohol and water, should be more dissociated than corresponding solutions of ammonium hydroxide. Indeed, a solution of sodium or potassium hydroxide, in alcohol alone, should manifest some dissociation, since, as stated above, it gives the color reaction with phenolphthaleïn.

All of these points were tested, experimentally, by the conductivity method, with the result that the theory of electrolytic dissociation was entirely confirmed.

This experiment furnishes a satisfactory lecture demonstration of the dissociating action of water. A few drops of an alcoholic solution of phenolphthaleïn are placed in a glass cylinder, and diluted to, say, 50 cc. by the addition of alcohol. A few drops of an aqueous solution of ammonia are then added. A red color may appear where the aqueous ammonia first comes in contact with the alcoholic solution of phenolphthaleïn, but this will disappear, instantly, on shaking the cylinder, leaving the solution with a yellowish tint, possibly due to the formation of the ammonium salt of phenolphthaleïn. Water is then gradually added to the cylinder, when the red color will appear, at first faint, then stronger, as the amount of water increases. When the red color has become intense, add a considerable volume of alcohol, and the entire color will disappear, leaving the solution slightly yellow again.

The experiment serves, then, not only to illustrate the dissociating action of water, but the driving back of the ions into molecules by alcohol.

**Conductivity is Additive. The Law of Kohlrausch.** — It has been shown by Kohlrausch, that the conductivity of solutions of electrolytes is an additive property of the ions which take part in carrying the current. Indeed, the law of Kohlrausch, of the independent migration velocity of the ions, is but another expression of this fact. It is well known that the law, in the form stated by Kohlrausch, holds only for great dilutions, in which dissociation is complete. Ostwald[1] has pointed out that the law holds for any dilution, provided that we take into account the amount of the dissociation at that dilution. This is obviously necessary, since it is only the dissociated molecules which take part in the conductivity. If we represent the percentage of dissociation, or the activity coefficient, by $\alpha$, the law of Kohlrausch becomes: —

$$\lambda \quad \mu = \alpha(u + v),$$

$u$ depending upon the cation, $v$ upon the anion. The law in this form is applicable to all solutions of electrolytes, and illustrates, also, the additive property of conductivity.

A number of other properties could be adduced in evidence of the general principle, that the properties of completely dissociated solutions are additive, being the sum of the properties of the ions; but those already considered are quite sufficient. The theory of electrolytic dissociation is here entirely substantiated by the facts. And these facts would be very difficult to explain without some such conception as that with which we are now dealing.

[1] Lehrb. d. allg. Chem. II, p. 673.

## PROPERTIES OF COMPLETELY DISSOCIATED, AND OF UNDISSOCIATED MIXTURES

**Mixture of Two Completely Dissociated Compounds.** — The theory of electrolytic dissociation leads to some interesting conclusions, in the case of mixtures of completely dissociated substances, and these conclusions can be tested experimentally. Let us take the case of two salts which are completely dissociated at moderate dilutions, say, sodium chloride and potassium bromide. We would have in the solution only the ions into which these compounds had dissociated: —

$$NaCl = \overset{+}{Na} + \overset{-}{Cl};$$

$$KBr = \overset{+}{K} + \overset{-}{Br}.$$

We would have sodium and potassium cations, and chlorine and bromine anions. All the properties of such a mixture would be a function of the properties of these ions.

Suppose we were now to prepare a mixture of potassium chloride and sodium bromide, which was completely dissociated. We would have in the solution: —

$$KCl = \overset{+}{K} + \overset{-}{Cl};$$

$$NaBr = \overset{+}{Na} + \overset{-}{Br},$$

potassium and sodium cations, and chlorine and bromine anions. But these are exactly the same ions which we had in our first mixture.

We are led to the conclusion, that if we use gram-

molecular weights of both substances in each case, we will have exactly the same number of the same kinds of ions in the two solutions. And since the properties of a completely dissociated solution depend only upon the properties of the ions present, the properties of these two mixtures must be the same. If, then, we mix a gram-molecular weight of sodium chloride with a gram-molecular weight of potassium bromide, and dilute the solution of the two until both are completely dissociated, this mixture must have exactly the same properties as that prepared by mixing a gram-molecular weight of potassium chloride with a gram-molecular weight of sodium bromide, and diluting the solution to the same point as the first. This is the conclusion to which we are led by our theory. What are the facts? The facts confirm this conclusion absolutely. All of the properties of the two mixtures have been found to be exactly the same. The two solutions resemble one another as closely as the two halves of the same solution.

**Mixture of Two Completely Undissociated Compounds.** — The conclusion to which we are led in the case of completely dissociated compounds does not obtain at all for undissociated substances. Indeed, in the latter case, we are led by the theory to exactly the opposite conclusion. Take two undissociated substances — say methyl chloride and ethyl bromine — and dissolve the mixture; we will have only molecules of the two substances present. The properties of this mixture will be a function of the properties of these two kinds of molecules.

Then, mix methyl bromide and ethyl chloride, we will have only these two kinds of molecules present, and

the properties of the mixture will be a function of the properties of the molecules which are in the mixture.

But in the first mixture we have molecules of methyl chloride and ethyl bromide, in the second, of methyl bromide and ethyl chloride. And since we have different kinds of molecules in the two mixtures, the properties of the two must be different.

If, then, we mix gram-molecular weights of methyl chloride and ethyl bromide, the mixture must have different properties from a corresponding mixture of gram-molecular weights of methyl bromide and ethyl chloride.

This is the conclusion to which we are led by the theory of electrolytic dissociation, and here again the facts are in perfect accord with the theory. It has been found, experimentally, that a mixture of methyl chloride and ethyl bromide has properties quite different from a corresponding mixture of methyl bromide and ethyl chloride.

Fact and theory thus agree, both when the constituents of the mixture are completely dissociated, and when they are not at all dissociated.

### HEAT OF NEUTRALIZATION IN DILUTE SOLUTIONS

If the theory of electrolytic dissociation is true, a dilute aqueous solution of a strongly dissociated compound contains only ions, as has been stated. A solution of a base contains the hydroxyl anion, and a cation whose nature depends upon the particular base used. A solution of an acid contains the hydrogen cation and an anion whose nature depends upon the acid chosen. Similarly, a solution of a salt is but a solution of anions and cations. In terms of the theory of electrolytic dissociation, the pro-

cess of neutralizing an acid by a base consists in the union of the hydroxyl anion of the base with the hydrogen cation of the acid, forming a molecule of water. The cation of the base and the anion of the acid remain in exactly the same condition after neutralization as before. Let us take an example.

A solution of hydrochloric acid is a solution of hydrogen cations and chlorine anions:—

$$HCl = \overset{+}{H} + \overset{-}{Cl}.$$

A solution of potassium hydroxide is a solution of potassium cations and hydroxyl anions:—

$$KOH = \overset{+}{K} + \overset{-}{OH}.$$

When the two solutions are brought together we have:—

$$\overset{+}{K} + \overset{-}{OH} + \overset{+}{H} + \overset{-}{Cl} = \overset{+}{K} + \overset{-}{Cl} + H_2O.$$

The potassium and chlorine are in exactly the same condition after neutralization as before, *i.e.* both are ions; while the hydrogen and hydroxyl are united, forming a molecule of water.

Neutralization of acids and bases is, then, in terms of the theory of electrolytic dissociation, nothing more than the union of the cation hydrogen and the anion hydroxyl to form a molecule of water.

How can this be tested experimentally?

If neutralization consists only in the formation of a molecule of water, then the neutralization of any acid by any base is the same process as the neutralization of any other

acid by any other base. Therefore, the heat liberated by neutralizing an equivalent of any acid by an equivalent of any base must always be the same, since it is the heat of formation of the same amount of water from the ions $\overset{+}{H}$ and $\overset{-}{OH}$. This can be tested directly by experiment. It is only necessary to measure the heat liberated when acids and bases are neutralized, and see whether this is the same for the different compounds.

The following tables of heats of neutralization will test this point: —

Strong Acids and Bases

| | | | |
|---|---|---|---|
| $HCl + NaOH$ | = 13700 cal. | $HCl + LiOH$ | = 13700 cal. |
| $HBr + NaOH$ | = 13700 cal. | $HCl + KOH$ | = 13700 cal. |
| $HNO_3 + NaOH$ | = 13700 cal. | $HCl + \frac{1}{2}Ba(OH)_2$ | = 13800 cal. |
| $HI + NaOH$ | = 13800 cal. | $HCl + \frac{1}{2}Ca(OH)_2$ | = 13900 cal. |

Weak Acid and Strong Base

| | |
|---|---|
| $CH_3COOH + NaOH$ | = 13400 cal. |
| $CHCl_2COOH + NaOH$ | = 14830 cal. |
| $H_3PO_4 + NaOH$ | = 14830 cal. |
| $HF + NaOH$ | = 16270 cal. |

The agreement between the heats of neutralization of the strong acids with the strong bases is striking, when we consider the necessary errors involved in thermochemical measurements.

The heats of neutralization of weak acids with a strong base differ very greatly from the constant obtained when both compounds are strongly dissociated.

In the application of the theory to the phenomenon of neutralization, it was assumed above, that both the acid and the base were completely dissociated. If, on the other hand, either acid or base is incompletely dissociated, then the heat set free when the two are brought together is not simply the heat liberated by the union of hydrogen and hydroxyl ions to form water, but this quantity, plus the heat of dissociation of that part of the acid or base which is undissociated.

This explains the difference between the amounts of heat liberated, when both the acids and bases are strong, and when either the acid or base is weak.

The theory of electrolytic dissociation is, then, strictly in accord with the facts, as far as the heat of neutralization is concerned. This applies not simply to the strong acids and bases, but to the apparently exceptional cases of the weakly dissociated compounds.

It will be observed, that in the above interpretation of the process of neutralization, it is assumed that all of the hydrogen and hydroxyl ions combine to form water. It has been shown by six separate lines of work, that whenever hydrogen and hydroxyl ions come together they combine and form water. This is the same as to say that water is undissociated. The apparent assumption is, therefore, well supported by the experimental facts.

**Hess's Law of the Thermoneutrality of Salt Solutions.** — A dilute aqueous solution of a salt is, in terms of our theory, a solution of ions. Thus, a dilute aqueous solution of potassium chloride contains only potassium and chlorine ions. Similarly, a dilute solution of sodium chloride is but a solution of sodium and chlorine ions. When the solutions

of the two salts are mixed, the mixture contains only potassium, sodium, and chlorine ions.

$$KCl \text{ in dilute aqueous solution} = \overset{+}{K} + \overset{-}{Cl}.$$

$$NaCl \text{ in dilute aqueous solution} = \overset{+}{Na} + \overset{-}{Cl}.$$

When the two solutions are mixed, we have:—

$$\overset{+}{K} + \overset{+}{Na} + \overset{-}{Cl} + \overset{-}{Cl},$$

and there should be no thermal change produced on mixing such solutions. It has long been known, that if completely dissociated solutions of neutral salts are mixed, there is neither evolution nor absorption of heat, provided that none of the ions unite to form molecules, or to form new complexes of ions. These facts are usually stated as Hess's law of the thermoneutrality of salt solutions, which but names them, without attempting an explanation.

The theory of electrolytic dissociation not only furnishes a reason for the law of the thermoneutrality of salt solutions, but makes it a necessary consequence of its own validity.

### OSMOTIC PRESSURE — LOWERING OF FREEZING-POINT — RISE IN BOILING-POINT — CONDUCTIVITY

It will be remembered that Arrhenius proposes the theory of electrolytic dissociation, to account for the abnormally large osmotic pressure shown by certain classes of substances. We may divide chemical compounds into two classes, with respect to their power to exert osmotic pressure: First, substances like the carbohydrates, alcohols, etc., *i.e.* the chemically inactive organic compounds, which exert an osmotic pressure that obeys the gas laws, and

will be called normal; second, the acids, bases, and salts, which exert a much greater osmotic pressure.

If we determine the freezing-point lowering produced by these substances, when dissolved in water, we will find that they again divide themselves into two classes; the organic compounds giving freezing-point lowerings which we will call normal, and the acids, bases, and salts, giving a greater depression of the freezing-point. All of those compounds, and only those, which show too great osmotic pressure, give too great lowerings of the freezing-point of water.

Furthermore, if we study the rise in the boiling-point of solvents produced by dissolved substances, we will find, again, that the organic compounds above referred to produce a certain rise in the boiling-point, while all the acids, bases, and salts produce a greater rise in boiling-point. Substances divide themselves here, as in the last two cases, into two classes, and it is exactly the same division as shown both by osmotic pressure, and lowering of freezing-point.

Finally, if we study the conductivity of solutions of chemical compounds, we will find that solutions of the neutral organic compounds do not conduct the current, while solutions of all acids, bases, and salts, do conduct. If we were to divide all chemical substances with respect to their power to conduct the electric current, they would again fall into two classes, and exactly the same two classes as were furnished by each of the above three properties. Substances which conduct the current are termed *electrolytes*, and those which do not conduct, *non-electrolytes;* so that we will now refer to these two classes of chemi-

cal compounds as, respectively, electrolytes and non-electrolytes.

We have, then, this very remarkable relation. All of those substances, and only those, which show abnormally great osmotic pressure, show abnormally great lowering of the freezing-point, rise in boiling-point, and conduct the current. These electrolytes, as we will see later, are also the most active chemically.

The converse is also true, that all of those substances, and only those, which show normal osmotic pressures, show normal lowering of freezing-point, rise in boiling-point, and do not conduct the current. These non-electrolytes, as we will also see, are the least active of chemical substances.

Having found this qualitative relation, it remains to see whether it is quantitative, — whether a substance which shows too great osmotic pressure produces a lowering of freezing-point, and rise in boiling-point, which is too great, by the same amount.

If the abnormally great osmotic pressure is explained by the dissociation of molecules into ions, so, also, must the abnormally great lowering of freezing-point, and rise in boiling-point, produced by electrolytes, as well as their conductivity, be due to the same cause. If the theory of electrolytic dissociation is true, there must be a quantitative relation between abnormal osmotic pressure, lowering of freezing-point, rise in boiling-point, and conductivity. If such a quantitative relation can be shown to exist, it would be a strong argument in favor of the theory we are considering. We will show that such a relation does exist.

**Relation between Osmotic Pressure and Lowering of Freezing-point.** — The relations between the four properties here considered will be pointed out, first experimentally, and then in part, theoretically.

De Vries[1] has measured the relative osmotic pressures of a number of solutions, using vegetable cells. Without going into the details of this method, the principle can be concisely stated. When some vegetable cells, containing colored protoplasm surrounded by a semipermeable membrane, are immersed in solutions which have a greater osmotic pressure than the contents of the cell, we can see the contents of the cell contracted to one side, due to the loss of water to the solution. If the solution in which the cell is immersed has the same osmotic pressure as the contents of the cell, no water will pass into or out of the cell, and it will present a normal appearance. If the solution has a smaller osmotic pressure than the contents of the cell, water will pass in, and the cell will be distended. By studying the behavior of the cell in the solution, under the microscope, we can determine whether the solution has a greater, less, or the same osmotic pressure as the contents of the cell. By starting with a solution which has a greater osmotic pressure than the contents of the cell, and diluting it gradually, we can determine, from the behavior of the cell, when its osmotic pressure is just equal to that of the contents of the cell. We can thus prepare solutions of different substances, having each the same osmotic pressure as the cell contents, and, therefore, all having the same osmotic pressure. Such solutions, which have the same osmotic pressure, were termed *isos-*

[1] Ztschr. phys. Chem., 2, 415.

*motic.* When these concentrations were expressed in molecular quantities, their reciprocal values were termed *isotonic coefficients.* These show, directly, the relative osmotic pressures of solutions of equal molecular concentration. The coefficients for a number of compounds, as compared with the molecular lowerings of the freezing-point, are given in the following table, taken directly from the work of De Vries.[1]

| Substance | Isotonic Coefficients multiplied by 100 | Molec. Low. of Freezing-point multiplied by 10 |
|---|---|---|
| $C_6H_{12}O_6$ | 181 | 185 |
| $C_{12}H_{22}O_{11}$ | 188 | 193 |
| $MgSO_4$ | 196 | 192 |
| $KNO_3$ | 300 | 308 |
| $K_2SO_4$ | 391 | 390 |
| NaCl | 305 | 351 |

These are just a few of the many cases given by De Vries. But they are sufficient to show the proportionality between isotonic coefficients and molecular lowering of the freezing-point for a number of classes of substances.

**Relation between Osmotic Pressure and Lowering of Vapor-tension. Rise in Boiling-point.** — In the same table in which the above relation is pointed out, De Vries also shows that a proportionality exists between the isotonic coefficients of a number of substances, and the molecular lowering of the vapor-tension; lowering of vapor-tension being used here, instead of rise in boiling-point, which is proportional to it. A few results taken from the table are given: —

[1] Ztschr. phys. Chem., 2, 427.

| Substance | Isotonic Coefficients multiplied by 100 | Lowering of Vapor-tension multiplied by 1000 |
|---|---|---|
| $C_4H_6O_5$ | 198 | 178 |
| $C_4H_6O_6$ | 202 | 188 |
| $NaNO_3$ | 300 | 296 |
| $K_2C_2O_4$ | 393 | 372 |
| $K_2SO_4$ | 391 | 351 |
| $CaCl_2$ | 433 | 517 |
| $K_3C_6H_5O_7$ | 501 | 499 |

The proportionality between osmotic pressure and lowering of vapor-tension, or rise in boiling-point, is at once apparent.

**Relation between Osmotic Pressure and Conductivity.** — De Vries also compared the osmotic pressure of solutions and their conductivity. He calculated the sum of the molecules and ions, on the one hand from osmotic pressure, on the other from conductivity, and then compared the two values to see how they agreed. He obtained the following results:[1] —

| Substance | Sum of Molecules and Ions calculated — From Isotonic Coefficients | From Conductivity |
|---|---|---|
| Non-conductors | | |
| $C_3H_8O_3$ | 100 | 100 |
| $C_6H_{12}O_6$ | 106 | 100 |
| $C_{12}H_{22}O_{11}$ | 101 | 100 |
| Conductors | | |
| $MgSO_4$ | 125 | 135 |
| $KNO_3$ | 176 | 180 |
| KCl | 181 | 187 |
| NaCl | 179 | 182 |
| $NH_4Cl$ | 182 | 185 |
| $K_2SO_4$ | 230 | 234 |

[1] Ztschr. phys. Chem., 3, 109; also *loc. cit.*

The agreement between osmotic pressure and lowering of freezing-point, rise in boiling-point, and conductivity, is as close as could be expected, when we consider the large experimental error involved in determining osmotic pressure, directly, by any method, and even in determining the relative osmotic pressure of solutions by the method of De Vries.

**Relation between Lowering of Freezing-point and Rise in Boiling-point.** — Raoult[1] has shown, purely empirically, that the lowerings of the freezing-point, produced by some eighteen salts, stand in the same relation to one another as the rise in boiling-point produced by these same compounds. The results are not tabulated, and, therefore, will not be given here.

**Relation between Lowering of Freezing-point and Conductivity.** — That a quantitative relation exists between these quantities, for any given substance, was shown by Arrhenius, when he proposed the theory of electrolytic dissociation. Some of the data which he brought forward to prove this point have already been given (p. 98). The agreement between the values of $i$, as calculated from freezing-point lowering and from conductivity, was only fairly close, because the freezing-point method at that time was in a crude state, and gave only approximate results.

The freezing-point method has now been greatly improved,[2] — a number of sources of error having been eliminated, — until it can be used to measure the value of the coefficient of dissociation, as it is termed, with considerable

[1] Compt. rend., 70, 1349 (1870).

[2] Jones, Ztschr. phys. Chem., 11, 110 and 529; 12, 623. Loomis, Wied. Ann., 51, 500; 57, 495; 60, 523. Raoult, Ztschr. phys. Chem., 27, 617.

accuracy. The values of $\alpha$ have been determined by Jones,[1] for a large number of dilutions of different substances, using the freezing-point method. These have been compared with the values of $\alpha$ for the same dilutions of the same substances, using the conductivity method. The following results are taken from the paper of Jones:—

| Compounds | Concentration | $\alpha$ from Conductivity | $\alpha$ from Freezing-point Lowering |
|---|---|---|---|
| NaCl | 0.001 | 98.0 | 98.4 |
| NaCl | 0.01 | 93.5 | 90.5 |
| NaCl | 0.1 | 84.1 | 84.1 |
| $BaCl_2$ | 0.001 | 93.9 | 94.2 |
| $BaCl_2$ | 0.005 | 87.9 | 87.6 |
| $BaCl_2$ | 0.05 | 75.3 | 77.7 |
| HCl | 0.002 | 100.0 | 98.4 |
| HCl | 0.01 | 98.9 | 95.8 |
| HCl | 0.1 | 93.9 | 88.6 |
| $H_2SO_4$ | 0.003 | 89.8 | 86.0 |
| $H_2SO_4$ | 0.005 | 85.4 | 83.8 |
| $H_2SO_4$ | 0.05 | 62.3 | 60.7 |
| KOH | 0.002 | 100.0 | 98.4 |
| KOH | 0.01 | 99.2 | 93.7 |
| KOH | 0.1 | 92.8 | 83.1 |
| $K_2CO_3$ | 0.003 | 92.0 | 96.6 |
| $K_2CO_3$ | 0.005 | 88.6 | 96.0 |
| $K_2CO_3$ | 0.05 | 71.9 | 77.5 |

The percentage of dissociation $\alpha$, as measured by the freezing-point method, agrees surprisingly well with the values obtained from conductivity. The slight differences which exist are probably due to the different temperatures

[1] Phil. Mag., 36, 483.

at which the two sets of measurements were made — conductivity being determined at 18°, and freezing-point lowering a little below 0°.

We have now demonstrated, by experiment, the quantitative relation which exists between osmotic pressure, lowering of freezing-point, rise in boiling-point, and conductivity. We will now give a mathematical demonstration of one or two of these relations.

**Connection between Osmotic Pressure and Lowering of Freezing-point, established by Thermodynamics.** — The connection between osmotic pressure and lowering of the freezing-point was deduced thermodynamically by van't Hoff,[1] in the paper to which reference has so often been made.

Van't Hoff showed that solutions in the same solvent, having the same freezing-point, are isotonic at that temperature. He applied this to dilute solutions, and was led to the conclusion that solutions which contain the same number of molecules in the same volume, and, therefore, from Avogadro's law, are isotonic, have also the same freezing-point. This was discovered experimentally by Raoult, and led to the expression "normal molecular lowering of the freezing-point." This means the lowering in degrees, produced by a gram-molecular weight of the substance in 100 grams of the solvent. This normal molecular lowering of the freezing-point, which we will term the freezing-point constant for the solvent, van't Hoff then derived from the latent heat of fusion of the solvent. This deduction has been developed more fully by Ostwald,[2]

[1] Harper's Science Series, IV, 29. Ztschr. phys. Chem. 1, 481.
[2] Lehrb. allg. Chem., I, p. 759.

and it will be given here essentially as worked out by him, with some slight changes[1] which seem to make the steps a little clearer.

Let us take a solution consisting of $n$ volumes of the dissolved substance and $N$ molecules of the solvent (molecule = gr.-molec. wt.). Let $T$ be the temperature of solidification of the solvent, and $\Delta$ the lowering of the freezing-point. Here as much of the solvent is allowed to solidify as would serve for the solution of one molecule of the substance, $= \frac{N}{n}$ molecules.

Let $\lambda$ be the latent heat of fusion of the solvent; the amount of heat liberated would be $\frac{N}{n}\lambda$. If, now, the ice is separated from the solution, warmed to temperature $T$, and melted, and finally allowed to mix with the solution by passing through a semipermeable membrane, it will exert an osmotic pressure $p$. If $v$ is the volume of the solvent which solidified, the work $= pv$, the heat $\frac{N}{n}\lambda$; from which:—

$$\frac{pvn}{N\lambda} = \frac{\Delta}{T}.$$

But $pv = RT$, and $R = 2$ cal. Substituting, we have:—

$$\Delta = \frac{n}{N}\frac{2\,T^2}{\lambda}.$$

Let $M$ be the molecular weight of the solvent, and substituting $N = \frac{100}{M}$, we have:—

$$\Delta = \frac{nM}{100}\frac{2\,T^2}{\lambda}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1] Jones, Phil. Mag., 36, 493.

In the Raoult formula $m = \frac{K}{A}$, $m$ is the molecular weight of the dissolved substance, $K$ is the freezing-point constant, and $A$ the specific lowering of the freezing-point. $A = \frac{\Delta}{p}$, where $\Delta$ is the lowering of the freezing-point observed, and $p$ the percentage concentration of the solution.

$$m = \frac{Kp}{\Delta}.$$

Let $n$ be the number of molecules of the dissolved substance in 100 g. of the solvent.

$$n = \frac{p}{m};$$

substituting, $$m\Delta = Kmn;$$

$$\Delta = Kn. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (1) and (2) $$K = \frac{M}{100} \frac{2\,T^2}{\lambda}.$$

If $L$ is the heat of fusion of 1 g. of the substance,

$$\lambda = LM.$$

Substituting, $$K = \frac{2\,T^2}{100\,L}.$$

From this equation van't Hoff has calculated the value of the freezing-point constant for a number of solvents, and compared these values with those found experimentally.

| Solvent | Constant calculated from $K = \frac{2\,T^2}{100\,L}$ | Constant found Experimentally |
|---|---|---|
| Water | 18.9 | 18.5 |
| Acetic acid | 38.8 | 38.6 |
| Formic acid | 28.4 | 27.7 |
| Benzene | 53.0 | 50.0 |
| Nitrobenzene | 69.5 | 70.7 |

The values of the freezing-point constant, as calculated from the van't Hoff formula, agree very satisfactorily with those found by experiment.

**Relation between Osmotic Pressure and Lowering of Vapor-tension (Rise in Boiling-point). Theoretical Demonstration.** — The relation between osmotic pressure and lowering of vapor-pressure has been derived in a simple manner by Arrhenius.[1] The line of reasoning is as follows: Given a vessel of the form shown in Fig. 5, closed at the bottom by a semipermeable wall. Let this vessel be filled with a solution $S$, and dip into a vessel containing the pure solvent $D$. The whole is covered with a bell-jar, and exhausted. Equilibrium will be established when the pressure of the column of liquid, from the surface of the solvent up to $h$, is equal to the osmotic pressure, and the free space is saturated by the vapor $D'$. When equilibrium is established, the vapor-pressure of the solution at $h$ must be just equal to the pressure of the vapor of the solvent at this point. If it were less, liquid would condense in $h$, if more, it would distil out of $h$, and there would not be equilibrium, since liquid would flow either out or in through the membrane. If $f'$ is the tension of the vapor of the solution at $h$, $f$ the vapor-tension of the solvent, $h$ the height of the column of liquid, and $d$ the density of the vapor in the bell-jar, we have: — $f' = f - hd.$

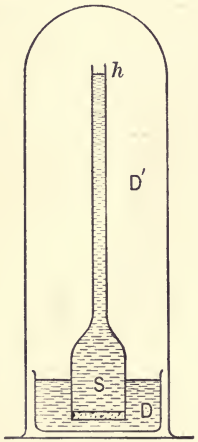

FIG. 5.

[1] Ztschr. phys. Chem., 3, 115.

*The value of h.* — Let us have a very dilute solution, in which $n$ gram-molecules of substance are contained in $g$ grams of solvent. From van't Hoff's law of osmotic pressure we would have: —

$$PV = RT \times n,$$

in which $P$ is the osmotic pressure of the solution, and $V$ its volume. Let $s$ be the specific gravity of both solution and solvent; they are practically the same for very dilute solutions.

$$P = h \times s;$$

$$V = \frac{g}{s}.$$

Substituting, $$PV = nRT = \frac{hsg}{s} = hg;$$

$$hg = nRT \therefore h = \frac{nRT}{g}.$$

*The value of d.* — Let $v$ be the volume of a gram-molecule of the vapor of the solvent $D$, and $f$ the pressure of this vapor: —

$$fv = RT,$$

$$v = \frac{RT}{f}.$$

If $M$ is the molecular weight of the solvent

$$d = \frac{M}{v},$$

$$\frac{M}{d} = \frac{RT}{f} \therefore d = \frac{Mf}{RT}.$$

Substituting the values, $h = \frac{nRT}{g}$ and $d = \frac{Mf}{RT}$ in the equation $f' = f - hd$, we have:—

$$f' = f - \frac{nRT}{g} \times \frac{Mf}{RT}$$

$$f' = f - \frac{nMf}{g},$$

or,
$$\frac{f - f'}{f} = \frac{nM}{g},$$

which is essentially Raoult's fundamental equation for the lowering of the vapor-pressure of a solvent by a dissolved substance. Raoult's equation, which has been amply verified by experiment, is usually written:—

$$\frac{f - f'}{f} = \frac{n}{N}$$

where $N$ is the number of gram-molecules of the solvent. It is evident that $N = \frac{g}{m}$ when the two equations become identical.

Theoretical demonstrations of other relations between the four properties of solutions, which we are considering, have been furnished. Thus, Guldberg [1] has proved a direct connection between lowering of freezing-point and lowering of vapor-tension. Arrhenius [2] has shown how freezing-point lowering and conductivity are connected, by calculating the value of the coefficient $i$ from both, and then showed, experimentally, that the two values agreed with

[1] Compt. rend., 70, 1349. [2] *Loc. cit.*

one another (see p. 98). A number of other demonstrations of relations between these properties could be given, did space permit, but quite enough has been developed to show, both experimentally and theoretically, that they are quantitatively connected. Whatever causes electrolytes to exert a greater osmotic pressure than non-electrolytes, also causes them to produce a greater lowering of the freezing-point, rise of boiling-point, and enables them to conduct the current.

Arrhenius showed that his theory explains all of the facts concerning osmotic pressure. From the above relations alone it must, therefore, accord with the facts connected with the other three properties. We have, however, an abundance of independent evidence, were this necessary, that the theory of electrolytic dissociation is in perfect harmony, not only with what is known of the osmotic pressure of dilute solutions, but with every other property possessed by them.

### EXPERIMENT TO SHOW THE PRESENCE OF FREE IONS

If only ions conduct, then, whenever a current is passed through a solution of an electrolyte, a movement of the ions is necessarily involved. The same applies to a solution of an electrolyte charged electrostatically. If the charging body is negative, it will attract the ions which carry the positive electricity in the solution, *i.e.* the cations, and will repel the anions. If the solution could then be separated into two parts, the one would contain an excess of cations, and the other an excess of anions.

**Illustration of a Solution charged Electrostatically.** — Let two vessels, $A$ and $B$, be filled with a solution of an electrolyte, say potassium chloride, and let the two be connected with a siphon filled with the same liquid. Let a negatively charged body $K$ be brought near to $A$; it will act by induction upon the system $AHB$. $A$ will become positive and $B$ negative. If now the siphon $H$ is removed, and then the body $K$, $A$ will remain positive and $B$ negative.

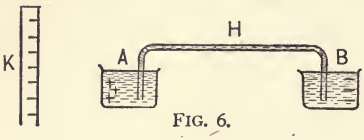

FIG. 6.

But, from the law of Faraday, electricity can move in solutions only by a movement of the ions. That $A$ should be positive, it is necessary that it should contain an excess of the potassium ions which carry the positive charge. Similarly, $B$ must contain an excess of chlorine ions. The number of these free ions in the solution must depend, of course, upon the intensity of the inducing action. To discharge $A$, introduce a platinum wire connected with the earth. The potassium ions give up their positive charge to the wire, and become atoms. These now act upon the water, forming potassium hydroxide, and hydrogen which escapes from the solution.

This experiment was proposed by Ostwald,[1] simply as an illustration. It is obvious to any one that, under conditions such as those described, the amount of hydrogen set free would be far too small to be seen. On account of the very great charge carried by an ion, the number of ions which would be induced from one vessel to the other, by the above arrangement, would be relatively small.

[1] Ztschr. phys. Chem., 2, 272.

The above experiment illustrates another point, as Ostwald has shown. That electrostatic charging of electrolytes takes place with enormous velocity, as with conductors of the first class. But Kohlrausch has shown that the ions move very slowly. If the above induction phenomenon takes place very rapidly in the solution, then the potassium ion, which brings the positive charge closest to *K*, could not have been connected with the chlorine ion, which takes the negative charge to the region most remote from *K*. Free ions must, therefore, be present in the solution at all times, or the electrolyte must be dissociated.

**Experiment of Ostwald and Nernst.** — The experiment described above, while theoretically correct, must be regarded as only an illustration. Ostwald and Nernst[1] have, however, devised an experiment, which they claim demonstrates to the eye the effect described by Ostwald. To be able to see the hydrogen liberated by induction, unusual precautions must be taken, because of the very small quantity of gas which will be set free. To liberate a milligram of hydrogen would require a condenser of about one square kilometre. But one milligram of hydrogen will fill 12 to 13 cubic centimetres, under ordinary conditions.

By means of a microscope, it is possible to see a bubble of gas 0.01 mm. in diameter, and this amount could be liberated, using a condenser of ordinary dimensions. The gas was collected in the capillary of a Lippmann electrometer, since a small quantity could be easily recognized in this way.

[1] Ztschr. phys. Chem., 3, 271 (1888).

The experiment of Ostwald and Nernst will now be described in detail.

A glass tube 30 to 40 cm. in length, provided with a stop-cock, was drawn out at one end to a fine capillary. The diameter of the capillary was such that, when the tube was filled with mercury, it would begin to flow out of the fine point. The tube was fastened upright, and its tip allowed to dip in dilute sulphuric acid. The mercury was then drawn up into the capillary, and the acid drawn in after it. By means of the stop-cock, the surface of contact between the mercury and the acid could be kept about the middle of the capillary. A platinum wire, fused into the glass tube, connected with the mercury.

A large glass flask was filled with dilute sulphuric acid. Its outer surface was covered with tinfoil, and its neck varnished with shellac. The contents of the flask were connected with the sulphuric acid into which the capillary tube dipped, by means of a moist cord. The glass flask was insulated, by placing it upon a plate of hard rubber. The outer coating on the flask was connected with the positive pole of a small machine for generating electricity; the mercury in the tube connected with the earth. When the machine was set in motion, the meniscus in the capillary rushed up with violence, and at the same time, several bubbles of gas separated, which broke the thread of mercury in a number of places. This is nearly the verbatim account of what happened, as given by the experimenters themselves.

They explain the facts as follows: "By charging the coating on the outside of the flask with positive electricity, the negative electricity in the interior is attracted and held,

while the positive is repelled. The latter passes through the thread, into the capillary electrode, and through the platinum wire in the latter to the earth. There is no closed current present; the entire movement of electricity which is produced is the result of induction."[1]

As the outer coating of the flask becomes charged with positive electricity, the ions $SO_4$, which carry the negative charge, are attracted, the positive ions, hydrogen, are repelled, pass over the moist cord to the mercury, give up their charge, and appear as ordinary hydrogen gas.

The objection could be raised to this experiment, that a movement of electricity takes place, electrolytically, through the glass, and that this causes the separation of the hydrogen. The authors performed a number of experiments to test this point, and convinced themselves that this is strictly an induction phenomenon.

They worked quantitatively, as far as possible, determining the amount of hydrogen which separates and the amount of the electricity induced, and found that the amount of gas liberated corresponded to that calculated from Faraday's law to within the limit of experimental error. They concluded that movement of electricity in electrolytes, corresponding to Faraday's law, can take place only with a simultaneous movement of the ions, and that in electrostatically charged electrolytes a number of ions, corresponding to the amount of electricity, are free.

The question still remains, whether the ions are not set free at the moment of the electrostatic charging, so that the separation of the electricities is accompanied by a kind of electrolysis in the interior of the liquid. Ostwald and

[1] Ztschr. phys. Chem., 3, 122.

Nernst point out, that Clausius[1] has shown, that the movement of electricity in electrolytes obeys the weakest electromotive impulses, which would not be possible if the electricity must first perform an appreciable amount of work. They then show that such an assumption is against the laws of thermodynamics.

If we consider all of the precautions which Ostwald and Nernst have taken, it seems that they have conclusively proved the point, that free ions exist in electrostatically charged electrolytes, and these are not set free at the moment of charging.

### THE OSTWALD DILUTION LAW

**Conductivity and Dilution.** — It is well known, that the power of solutions of electrolytes to conduct the current increases with the dilution. If we always deal with molecular quantities, and express the conducting power of solutions in terms of molecular conductivity, we will see at a glance, that this is always larger (with a very few exceptions)[2] the greater the dilution. The rate of increase with the dilution is comparatively slow for the good conductors, but much more rapid for the poorer conducting substances, such as the organic acids. The difference between the molecular conductivities of the good and poor conductors thus becomes less as the dilution increases. This agrees with the view of Arrhenius, that the strength of all acids which, as we shall see later, depends only upon the number of hydrogen ions present, is the same at infinite dilution, since at this dilution all acids are completely dissociated.

[1] Pogg. Ann., 101, 338. [2] Kablukoff, Ztschr. phys. Chem., 4, 429.

Ostwald[1] found from his own work, that the molecular conductivity of all monobasic acids passes through the same series of values, and if acids $A$ and $B$ have the same conductivities at dilutions $v$ and $v_1$, they will have the same conductivities at $av$ and $av_1$.

Having found such a general relation between the conductivities of solutions of different substances, it remains to discover the mathematical expression connecting dilution and conductivity. And since dissociation and conductivity are proportional, we would then have connected dilution and dissociation.

**Ostwald's Deduction.** — Ostwald[2] has pointed out, that since the laws of gas pressure apply to the osmotic pressure of dilute solutions of non-electrolytes, if Arrhenius's theory of electrolytic dissociation to account for the exceptions shown by electrolytes is true, we ought to be able to apply the formula for a partly dissociated gas to a partly dissociated solution.[3]

For the homogeneous system of one volume of a gas dissociating into two volumes of gaseous products, Ostwald[4] deduced the formula: —

$$R \log \frac{p}{p_1 p_2} = \frac{q}{T} + \text{const.}$$

$p$, $p_1$, and $p_2$ are the pressures of the original gas and of the decomposition products, respectively, $q$ is the heat of decomposition, $R$ is the gas constant, and $T$ the absolute temperature.

[1] Journ. prakt. Chem., 31, 433; Lehrb. allg. Chem., II, p. 653.
[2] Ztschr. phys. Chem., 2, 136, 276; 3, 170.
[3] See also Planck, Wied. Ann., 34, 147.
[4] Ztschr. phys. Chem., 2, 36; Lehrb. allg. Chem., II, p. 723 (1st edition).

If the temperature is constant, and neither of the decomposition products is present in excess, the above expression becomes:—

$$\frac{p}{p_1^2} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $p$ is the pressure of the original gas, and $p_1$ that of the decomposition products.

Turning now to solutions, we must deal with osmotic pressure instead of gas pressure. The osmotic pressure is proportional to the amount of substance present, and inversely proportional to the volume. Let $u$ be the mass of the undecomposed electrolyte, and $u_1$ the mass of the decomposition products; $v$ is the volume:—

$$p = \frac{u}{v}, \text{ and } p_1 = \frac{u_1}{v}.$$

Substituting these values in (1), we have:—

$$\frac{uv}{u_1^2} = \text{constant.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The amount of the dissociation products $u_1$ is equal to the relation between the conductivity at volume $v$ ($\mu v$), and the conductivity at infinite dilution ($\mu\infty$):—

$$u_1 = \frac{\mu v}{\mu\infty}.$$

The amount of the undissociated substance $u$ is the complement of $u_1$:—

$$u = 1 - \frac{\mu v}{\mu\infty}.$$

Substituting these values of $u$ and $u_1$ in (2) we have:—

$$\frac{\mu\infty(\mu\infty - \mu v)}{\mu v^2} v = \text{constant} \quad . \quad . \quad . \quad . \quad (3)$$

and this is the dilution law of Ostwald. This can, however, be simplified. If we represent the activity coefficient, or the amount of dissociation, by $\alpha$:—

$$\alpha = \frac{\mu v}{\mu \infty}.$$

Substituting this value in (3) and taking the reciprocal, we have:—

$$\frac{\alpha^2}{(1-\alpha)\, v} = \text{constant.} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Ostwald[1] proceeded at once to test his formula by experiment. The conductivity of a number of acids at different dilutions was measured, and the values of $\alpha$ calculated for these dilutions. These values of $\alpha$, together with the volumes of the different solutions $v$, (volume is the number of litres which contains a gram-molecular weight of the electrolyte), were inserted in equation (4), to ascertain whether $c$ came out a constant, over a fairly wide range of concentration.

ACETIC ACID

| $v$ | $\alpha$ | $c$ |
|---|---|---|
| 8 | 1.193 | 0.00180 |
| 16 | 1.673 | 0.00179 |
| 32 | 2.38 | 0.00182 |
| 64 | 3.33 | 0.00179 |
| 128 | 4.68 | 0.00179 |
| 256 | 6.56 | 0.00180 |
| 512 | 9.14 | 0.00180 |
| 1024 | 12.66 | 0.00177 |

[1] Ztschr. phys. Chem., 3, 170, 241, 369.

O-AMIDOBENZOIC ACID

| $v$ | $\alpha$ | $c$ |
|---|---|---|
| 64 | 2.03 | 0.00066 |
| 128 | 3.02 | 0.00074 |
| 256 | 4.54 | 0.00084 |
| 512 | 6.62 | 0.00092 |
| 1024 | 9.44 | 0.00096 |

The values obtained for $c$, for most of the acids investigated, approached a constant. Ostwald studied between two and three hundred organic acids, and while there are a number of cases where $c$ did not come out very constant, yet it can be said, in general, that the law holds approximately for this class of substances. It should be said, that the organic acids are weakly dissociated compounds.

Bredig,[1] in studying the conductivity of ammonia, the amines, and other weakly dissociated bases, applied the Ostwald formula to somewhat more than thirty of these compounds.

| AMMONIA | | TRIPHENYLMETHANE | | PIPERIDINE | |
|---|---|---|---|---|---|
| $v$ | $c$ | $v$ | $c$ | $v$ | $c$ |
| 8 | 0.0023 | 8 | 0.0069 | 8 | 0.157 |
| 32 | 0.0023 | 32 | 0.0075 | 32 | 0.162 |
| 64 | 0.0023 | 64 | 0.0076 | 64 | 0.150 |
| 256 | 0.0024 | 256 | 0.0074 | 256 | 0.152 |

The values of $c$ (for each compound) are more nearly constant in the work of Bredig on the weak bases, than in that of Ostwald on the weak acids.

[1] Ztschr. phys. Chem., 13, 329.

While the dilution law of Ostwald holds fairly well for the weakly dissociated acids and bases, it does not apply at all satisfactorily to the strongly dissociated electrolytes — the strong acids and bases, and salts of these acids and bases. The reason for this failure on the part of Ostwald's law is yet to be discovered.

**Rudolphi's Dilution Law.** — Rudolphi,[1] from a study of the conductivity of solutions of silver nitrate of varying concentrations, discovered a new relation, which obtains for the strongly dissociated compounds. If we represent the volume by $v$, and the constant by $c$, as above, he found that when he applied the Ostwald equation to solutions of silver nitrate, he obtained the following values: —

$$\text{For } v = 16, \quad c = 0.26.$$

$$\text{For } v = 64, \quad c = 0.13.$$

$$\text{For } v = 256, \quad c = 0.065.$$

A glance at these figures will show that a real constant would be obtained, if the values of $c$ were multiplied by the square root of $v$ in each case; thus: —

$$0.26 \times \sqrt{16} = 0.13 \times \sqrt{64} = 0.065 \sqrt{256}.$$

We must, then, substitute for $v$, in the Ostwald expression, the square root of $v$, when it becomes: —

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v}} = \text{constant}.$$

Rudolphi applied his equation to between fifty and sixty strongly dissociated compounds, and the values found for $c$ approached a constant. While marked devia-

[1] Ztschr. phys. Chem., 17, 385.

tions are not wanting, yet Rudolphi's expression applies as well to the strongly dissociated electrolytes, as that of Ostwald to those which are less strongly dissociated, as the organic acids and bases. This will be seen from the following examples: —

| Hydrochloric Acid | | Potassium Sulphite | | Potassium Acetate | |
|---|---|---|---|---|---|
| $v$ | $c$ | $v$ | $c$ | $v$ | $c$ |
| 2 | 4.36 | 2 | 0.453 | 2 | 1.24 |
| 4 | 4.45 | 8 | 0.454 | 100 | 1.19 |
| 8 | 5.13 | 32 | 0.455 | 1,000 | 1.18 |
| 16 | 5.13 | 128 | 0.544 | 10,000 | 1.03 |

The Rudolphi expression is, of course, purely empirical. The physical significance of the $\sqrt{v}$ is thus far entirely unexplained. One or two modifications[1] of the Rudolphi formula have been proposed, but these are also empirical, and cannot be regarded as essentially in advance of the original.

We thus have two expressions for the relation between the dissociation of electrolytes and the dilution of the solution: That of Ostwald, which has a mathematical basis, and whose physical significance is known, applying to the weakly dissociated electrolytes; and that of Rudolphi, which is purely empirical, and whose physical meaning is unknown, applying to the strongly dissociated electrolytes. The relation between gaseous and electrolytic dissociation is thus established, as far as the less strongly dissociated electrolytes are concerned; but when the dissociation is nearly complete at moderate dilutions, there exists a discrepancy which still remains to be explained.

[1] Van't Hoff, Ztschr. phys. Chem., 18, 300; Kohlrausch, *ibid.*, 18, 662.

## EFFECT OF AN EXCESS OF ONE OF THE PRODUCTS OF DISSOCIATION

**Further Relation between Dissociation by Heat and Electrolytic Dissociation.** — It is well known that the dissociation of a vapor by heat is diminished by the presence of an excess of any of the products of dissociation. Thus, the vapor of ammonium chloride is more stable in the presence of an excess of ammonia, or of hydrochloric acid. And the vapor-density of phosphorus pentachloride, which breaks down by heat into phosphorus trichloride and chlorine, when determined in an atmosphere of chlorine, agrees very nearly with the theoretical density. Many such examples have been brought to light by the work of Deville and others.

It would be an interesting analogy, if we could find a similar effect in the case of electrolytic dissociation.

It has long been known, that when a saturated solution of sodium chloride is treated with gaseous hydrochloric acid, the gas dissolves and sodium chloride separates. A saturated solution of the salt contains sodium chloride molecules, sodium ions, and chlorine ions. When gaseous hydrochloric acid dissolves in the solution, it dissociates into hydrogen ions and chlorine ions. We have thus added one of the products of dissociation of the original compound, — chlorine ions. The dissociation of the sodium chloride is diminished, which is shown by the fact that some of the ions combine to form molecules, and these are precipitated from the solution.

The same relation is shown by Nernst[1] in the case of

[1] Ztschr. phys. Chem., 4, 375.

potassium chlorate. If to a saturated solution of potassium chlorate, either potassium or $ClO_3$ ions are added, some of the potassium chlorate will be precipitated. Thus, if to a saturated solution of potassium chlorate, either potassium chloride or potassium hydroxide is added, there will soon result a precipitation of potassium chlorate. If, on the other hand, sodium chlorate is added to a saturated solution of potassium chlorate, some of the potassium chlorate will be precipitated. This is at least qualitatively analogous to what takes place in the dissociation of a vapor by heat. It remains to study this effect quantitatively.

The theory of the mutual effect of salts on each other's solubility was developed by Nernst,[1] from the theory of electrolytic dissociation and the law of mass action. If the electrolyte is completely dissociated into two ions, the product of the active masses must be constant, and equal to the square of the solubility of the salt before any second compound is added. If $m$ is the solubility of the salt after a second salt with a common ion is added, $x$ the amount added, and $m_0$ the solubility of the salt alone, we have: —

$$m(m + x) = m_0^2.$$

But since the solutions are only partly dissociated, we must take into account the amounts of dissociation. Let $\alpha_0$ be the dissociation of the original substance in a saturated solution, $\alpha_1$ the dissociation of this substance in the presence of the substance added, and $\alpha$ the dissociation of the added substance; the above expression then becomes: —

[1] Ztschr. phys. Chem., 4, 379.

$$m\alpha(m\alpha + x\alpha_1) = m_0^2\alpha_0^2.$$

The effect of one salt on the solubility of another with a common ion was tested experimentally by A. A. Noyes.[1] He worked with eleven pairs of substances, determined the solubility of the one with which the solution was saturated, added the second, and determined the change produced in the solubility. He then calculated the solubility of the first salt, after the second was added, from the formula of Nernst, and compared the solubility found with that deduced theoretically. There is a general agreement between the two sets of values, but some discrepancies appeared, which are larger than could be accounted for by experimental error.

In calculating solubility from the equation of Nernst, we must know $\alpha$, $\alpha_1$, and $\alpha_0$, or the dissociations of all the solutions involved. Noyes concluded from his work that the deduction of Nernst is perfectly correct, and that the apparent differences are due to errors in the determination of the dissociation values. The relation between dissociation by heat and electrolytic dissociation, as effected by an excess of either of the products of dissociation, is, therefore, established.

**Determination of Electrolytic Dissociation by Change in Solubility.**—The slight differences between the solubilities found experimentally and calculated, led Noyes to suspect that the conductivity method of measuring dissociation was not accurate. He, therefore, reversed the above procedure, and used solubility measurements to determine dissociation. Knowing the dissociation of the substance in the

[1] Ztschr. phys. Chem., 6, 241.

saturated solution, and the change in the solubility of this substance produced by adding a given amount of the second substance, he could calculate the dissociation of the second substance.

A condition which must be fulfilled is, that the salt with which the solution is saturated is not very soluble, since we would then be dealing with a concentrated solution, to which the laws here involved do not apply.

Noyes first used thallous chloride with which to saturate his solvent, since it is not very soluble; and then added to this a number of soluble chlorides, as potassium, sodium, and ammonium, and calculated the dissociation of the latter, from the change which he found produced by them in the solubility of the thallous chloride. He[1] at first obtained dissociation values for the alkaline chlorides and other compounds, which differed considerably from that calculated from conductivity.

**Agreement between Dissociation determined by Conductivity, Freezing-point Lowering, and Solubility.** — We had, then, two methods of measuring electrolytic dissociation, conductivity, and change in solubility, and the two gave values which did not agree. The question arose, which is correct, or are both methods to be discarded?

At this time H. C. Jones[2] undertook, at the suggestion of Ostwald, to so improve the freezing-point method of Beckmann, that it could be applied to the measurement of electrolytic dissociation. A thermometer divided into thousandths of a degree was made, and carefully standardized. The apparatus to contain the liquid was enlarged

[1] Ztschr. phys. Chem., 9, 603; 12, 162; 13, 412.
[2] *Ibid.*, 11, 110, 529; 12, 623.

so as to hold a litre. The air-bath around the liquid was enlarged, and a number of precautions taken to secure more accurate determinations of the temperatures at which both solvent and solution froze. The dissociation of a number of acids, bases, and salts was worked out by this improved freezing-point method, over a considerable range of concentration. The result was, as has already been seen (p. 130), a satisfactory agreement between the dissociation calculated from freezing-point lowering and that calculated from conductivity.

In calculating dissociation from solubility, Noyes had assumed that the thallous chloride was dissociated to the same extent as potassium and sodium chlorides. He afterwards found[1] that this assumption was not correct. He determined the dissociation of thallous chloride, and when he introduced the correct values for this compound into the calculation, he found that the dissociation of the second compound, as determined by solubility, agreed very satisfactorily with the results of the other two methods.

The three most general methods of measuring electrolytic dissociation give, then, values which agree very well with one another. This fact should be carefully borne in mind, in considering the evidence bearing upon the theory of electrolytic dissociation.

**The Relation between the Two Kinds of Dissociation an Analogy.** — The relation which has just been pointed out, between the dissociation of a vapor by heat and electrolytic dissociation, is only an analogy. The processes are not at all identical, as is shown by the fact that the

[1] Ztschr. phys. Chem., 16, 125.

end products are very different. Take the compound ammonium chloride; it is broken down by heat into ammonia and hydrochloric acid: —

$$NH_4Cl = NH_3 + HCl.$$

Both of these are in the molecular condition, and can be isolated.

When ammonium chloride is dissociated electrolytically by water, it breaks down thus: —

$$NH_4Cl = \overset{+}{N}H_4 + \overset{-}{Cl}.$$

The composition of the products is not only different from the first case, but both the ammonium and chlorine exist as ions, the one charged positively and the other negatively, and neither can be isolated as such. That there is some deep-seated connection between the two processes is probable. Fused salts often conduct the current just as they would do if dissolved in water. But we must leave it for the future to show the exact nature of the connection between the two kinds of dissociation.

### DISSOCIATION AND CHEMICAL ACTIVITY

Perhaps the most interesting test of the theory of electrolytic dissociation yet remains. If the properties of dilute solutions of electrolytes are, in general, properties of the ions, what must be said in reference to the property of such solutions to react chemically. If there are only ions present in the solutions, it is clear that any chemical reaction which may take place is a reaction between ions only. If the solution contains molecules as well as ions,

the chemical reactivity may be due to the molecules, or it may be due to the ions, or it may be due to both. The problem is not only of interest from the physical chemical, but is of the very highest importance from the purely chemical, standpoint.

The number of possible cases by which the relation between dissociation and chemical activity can be investigated is very large. We will take several acids, inorganic and organic, and a few bases which have been worked out thoroughly in this connection. The method of attacking the problem is comparatively simple. The dissociation of substances must be determined, also their power to react chemically. Then the two must be compared.

**Conductivity and Reaction Velocity.** — Here, again, we are indebted for our knowledge chiefly to Ostwald. In a paper on the catalysis of methyl acetate,[1] he expressed the opinion that the velocity with which acids would invert cane-sugar, like other reactions of acids, depends only on their affinity. In a later paper,[2] describing work along this line, this view was substantiated. It then remained to determine whether there was any relation between these two reactions produced by different acids, and the dissociation of the acids themselves. The following table, taken from Ostwald's Lehrbuch,[3] gives a direct comparison of the conductivities of a number of acids, with their power to saponify methyl acetate, and to invert cane-sugar.

Column I gives the conductivities of the acids referred to hydrochloric acid as 100; column II, the velocities with which they effect the catalysis of methyl acetate; and

[1] Journ. prakt. Chem. [2], 28, 495. [2] *Ibid.*, 29, 385.
[3] Lehrb. allg. Chem., II, p. 650.

column III, the velocities with which they invert cane-sugar.

| | I | II | III |
|---|---|---|---|
| Hydrochloric acid, | 100.00 | 100.00 | 100.00 |
| Hydrobromic acid, | 101.00 | 98.00 | 111.00 |
| Nitric acid, | 99.60 | 92.00 | 100.00 |
| Sulphuric acid, | 65.10 | 73.90 | 73.20 |
| Formic acid, | 1.68 | 1.31 | 1.53 |
| Acetic acid, | 0.42 | 0.34 | 0.40 |
| Monochloracetic acid, | 4.90 | 4.30 | 4.84 |
| Dichloracetic acid, | 25.30 | 23.00 | 27.10 |
| Trichloracetic acid, | 62.30 | 68.20 | 75.40 |
| Oxalic acid, | 19.70 | 17.60 | 18.60 |
| Malonic acid, | 3.10 | 2.87 | 3.08 |
| Succinic acid, | 0.58 | 0.50 | 0.55 |
| Malic acid, | 1.34 | 1.18 | 1.27 |
| Tartaric acid, | 2.28 | 2.30 | — |
| Racemic acid, | 2.63 | 2.30 | — |

Ostwald adds, that when we consider that neither the temperature, nor the dilution, is the same in the three series, the agreement is satisfactory.

Ostwald studied also other reactions in which acids are involved, such as the velocity with which they dissolve calcium oxalate, or the way in which they divide a base between them. He found, in all of these cases, exactly the same order of avidity as given above.

A little later he carried out an investigation strictly analogous to the above, using a number of bases. The reaction studied was the velocity with which bases saponify ethyl acetate. The relative reaction velocities and conductivities are given in the following table. Column I gives the reaction velocities; column II, the conductivities.

| | I | II |
|---|---|---|
| Potassium hydroxide, | 161.00 | 161.00 |
| Sodium hydroxide, | 162.00 | 149.00 |
| Lithium hydroxide, | 165.00 | 142.00 |
| Ammonium hydroxide, | 3.00 | 4.08 |
| Methylamine, | 19.00 | 20.02 |
| Ethylamine, | 19.00 | 20.05 |
| Propylamine, | 18.06 | 18.04 |
| Amylamine, | 4.00 | 6.09 |
| Dimethylamine, | 22.00 | 23.05 |
| Diethylamine, | 26.00 | 28.03 |
| Trimethylamine, | 7.03 | 9.07 |
| Triethylamine, | 22.00 | 20.02 |
| Tetraethyl ammonium hydroxide, | 131.00 | 128.00 |

The agreement is as satisfactory as the conditions of work would allow us to expect.

**Dissociation measured by Chemical Activity.** — We have just seen that there is proportionality between dissociation and chemical activity, and that, therefore, the amount of dissociation may be used as a measure of the chemical activity of electrolytes.

This process can, on the other hand, be reversed, and the chemical activity of substances be used as a measure of their electrolytic dissociation. The conductivity and freezing-point are the most convenient and general methods for measuring electrolytic dissociation, but there are cases to which neither of these can be applied. It is sometimes desired to know the amount of the dissociation of some acid, in the presence of other electrolytes like the salts. Since all of the electrolytes present would take part in the conductivity, and in the lowering of the freezing-point of the solvent, it would be difficult, if not impossible, to deter-

mine the amount of the dissociation of the acid by means of either of these methods.

Some method must be employed which will detect one kind of ions in the presence of others. The chemical reactivity of the hydrogen ion has been made use of to solve the above problem. The rate at which cane-sugar is inverted by hydrogen ions can be determined very easily, and this reaction has been used by Trevor,[1] and others, to measure the number of hydrogen ions present.

Similarly, the specific chemical reactions of other ions have been used to determine the amount of these which are present, when more direct methods are not applicable. Thus, the dissociation of bases can be measured by the rate at which the hydroxyl ions saponify an ethereal salt. These examples suffice to show the proportionality between dissociation and chemical activity, and that either may be used as a measure of the other.

**Chemical Reactions usually take place between Ions.** — The facts just pointed out show that chemical reactions, in which acids and bases are involved, are reactions effected by ions. The number of reactions in which ions are known to take part is very great, including by far the majority of the cases with which we have to deal.

It has been supposed that gases do not conduct electricity, and are, therefore, undissociated. Reactions between gases could not be ionic, if this were true. The recent work of J. J. Thomson[2] has made it very probable that gases are dissociated, to some extent, and reactions between gases may be reactions between ions only. Thomson[3] has also shown that atoms of elementary hydrogen

[1] Ztschr. phys. Chem., 10, 321. [2] Nature, *loc. cit.* [3] *Ibid.*

gas behave as if they were both positive and negative, so that it is not improbable that reactions between the parts of elementary gases are ionic, but this is far from proved. It is not safe to conclude, at present, that all chemical reactions take place between ions. There are cases known of substances which conduct very little, or do not conduct at all, and yet react chemically. We have well characterized chemical compounds, formed by the union of two parts of the same general electrical character. Thus, phosphorus and chlorine, sulphur and chlorine, chlorine and bromine, chlorine and iodine, iodine and bromine, combine; and we are accustomed to regard all of these ions as carrying a negative charge. But in this connection the question arises, whether anion and cation are not, after all, only relative, one ion being charged more or less positive, or negative, than another.

Reactions between organic compounds, in general, take place much more slowly than between inorganic, and the former are much less dissociated. This is probably due to a slow progressive dissociation of the organic substances, as the ions already present enter into chemical combination. This raises the question, whether in those reactions between apparently undissociated substances, there are not a few ions present which react, and as these take part in the reaction, more and more ions are slowly formed, which then in turn react.

Whatever may be the final decision as to whether molecules can take part in chemical reaction, we are now justified in stating, that most of the chemical reactions with which we have to do are not reactions between molecules, but between ions.

**Dissociating Power of Different Solvents.** — Different solvents have very different powers of breaking down electrolytes into ions. Water is the strongest dissociant known. Of the more common solvents, formic acid stands next to water in its ionizing power. Then come methyl alcohol and ethyl alcohol, respectively, then acetone, and finally the ethereal salts and hydrocarbon, which have very slight dissociating power.

J. J. Thomson[1] has worked out an ingenious theory, which will be considered later, connecting the dissociating power of solvents with their dielectric constants. Experiment has shown, that there is undoubtedly a qualitative relation between the two, but there does not seem to be a proportionality. This is shown by recent work on the dissociating power of formic acid,[2] and of methyl and ethyl alcohols.[3] While the dissociating powers are in general in the same order as the dielectric constants, they are not proportional to them.

If water has such remarkable dissociating power, and as chemical activity is due chiefly to ions, water should play a very prominent rôle in bringing about chemical reaction. We will now examine a number of cases which will show whether this is true.

### EFFECT OF WATER ON CHEMICAL ACTIVITY

Unless very special precautions are taken to exclude moisture, every chemical reaction takes place in the presence of water. This is largely due to the presence of water-vapor in the air, which permeates everything with

[1] Phil. Mag., 36, 320. [2] Zanninowich-Tessarin, Ztschr. phys. Chem., 19, 251.
[3] Jones, Ztschr. phys. Chem. Jubelband.

which it comes in contact. Further, when a solvent other than water is used, water is often formed as one of the products of the many reactions. If there was a trace of water-vapor present to start the reaction, the quantity would increase rapidly as the reaction progressed.

To study the effect of water on chemical activity, we must exclude all traces of moisture at the outset, and choose reactions in which no water is formed. We must see how the reaction progresses in the absence of water, then admit water, and see what difference is produced. This is the method which has been employed, and it has led to some highly interesting and surprising results. Some of these will now be taken up.

**Action of Dry Chlorine on Metals.** — Wanklyn[1] passed dry chlorine over fused metallic sodium, and found that no action resulted. The melted sodium was shaken in contact with the chlorine, so as to expose a fresh surface of the metal. Still there was no chemical action between the two. This explains the frequent failure of the lecture experiment, where sodium chloride is formed by the direct union of sodium and chlorine. If the lecturer is careful to dry the chlorine gas which is passed over the molten metal, he usually observes the sodium lying in the same condition after the experiment as before. But if moisture in any way is admitted, the reaction takes place with violence.

Comper[2] studied the action of dry chlorine on a number of metals. He found that metallic zinc was not acted on by the chlorine at first, but the thin zinc-foil was attacked after a time. Metallic magnesium was not acted upon at

[1] Chem. News, 20, 271 (1869). [2] Journ. Chem. Soc., 43, 153 (1883).



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all, and metallic silver very slowly. Bismuth was apparently unacted upon, but tin was rapidly attacked. Antimony and arsenic were rapidly acted upon, while mercury was acted upon as rapidly as by moist chlorine.

In these experiments the chlorine was dried over calcium chloride for some days. This was, evidently, not sufficient to remove the last traces of moisture, so that the chlorine used by Comper was only partly freed from water-vapor. It would be of interest to repeat these experiments with perfectly dry chlorine.

**Comparative Inactivity of Dry Oxygen.** — H. B. Baker[1] carried out a number of experiments with carefully dried oxygen, which led to results of very considerable importance. The gas was dried by allowing it to stand for a long time in the presence of phosphorus pentoxide. Moist carbon, in the presence of oxygen, burned with the scintillation characteristic of this reaction. A certain amount of the dried carbon was burned in dry oxygen, but much less than of the moist, and there was no scintillation in the dry oxygen. Baker concluded from a number of experiments, that pure charcoal, heated in oxygen dried over phosphorus pentoxide, does not burn with a flame; partial combustion, however, goes on, both carbon monoxide and carbon dioxide being formed. Sulphur, boron, amorphous and ordinary phosphorus, do not burn in dry oxygen. Selenium, tellurium, arsenic, and antimony show no difference in their combustion, whether the oxygen be moist or dry.

Dixon[2] studied the action of dry oxygen on carbon monoxide, under the influence of the spark. He mixed

[1] Phil. Trans. (1888), 571.

[2] *Ibid.* (1884), 617.

three volumes of carbon monoxide and one volume of dry oxygen, and passed a spark through the mixture. There was no explosion. More oxygen was then added, and again the spark passed without explosion.

A fresh charge of carbon monoxide was then prepared from oxalic acid, and an excess of dry oxygen mixed with it. The spark passed through this, also, without any explosion. A drop of water was then added to the mixture, the spark passed and there resulted the usual explosion.

Experiments were then carried out to determine the velocity of the reaction, as affected by the amount of steam present. By the addition of steam it was found that the velocity of the reaction increased very rapidly. The conclusions from this work were: The drier the carbon monoxide and the oxygen, the less the tendency to unite; a trace of aqueous vapor causes the mixture to become inflammable, and the velocity of the reaction increased with the amount of water present.

**Dry Hydrochloric Acid does not decompose Carbonates.** — After Wanklyn had showed that dry chlorine would not act on fused sodium, and Baker, that dry oxygen is comparatively inactive, it was of interest to test the chemical behavior of other substances when free from moisture. One of the most vigorous of chemical reactions is the decomposition of carbonates by strong acids. Hughes[1] studied the behavior of dry hydrochloric acid toward carbonates, to see what influence moisture would have in such a reaction.

Hydrochloric acid gas was dried, by passing it over sulphuric acid and then over phosphorus pentoxide. It

[1] Phil. Mag., 34, 117 (1892).

was then brought in contact with carefully dried calcium carbonate. A few results will show the amount of carbonate decomposed. In one experiment: —

| | |
|---|---|
| Amount of carbonate used | 0.8705 g. |
| Weight of carbonate after treating with dried hydrochloric acid | 0.8712 g. |
| Increase in weight | 0.0007 g. |
| Percentage increase | 0.08 |

In a second experiment the percentage increase in weight was 0.1. The theoretical increase in weight for complete transformation is 29 per cent.

Moist hydrochloric acid gas was then passed over calcium carbonate for the same length of time, when more than one hundred times as much carbonate was decomposed as when dry hydrochloric acid gas was used. The experiment was then performed just as above, using witherite ($BaCO_3$) instead of calcite. The result of one experiment is given: —

| | |
|---|---|
| Amount of witherite used | 0.9976 g. |
| Weight after treating with dried hydrochloric acid gas | 0.9984 g. |
| Increase in weight | 0.0008 g. |
| Percentage increase | 0.08 |

The theoretical increase in weight, if all of the carbonate is transformed into chloride, is 14.7 per cent.

Hughes concluded from his work, that the increase in the weight of the carbonate, after passing a stream of dry hydrochloric acid over it, was so small, that no definite proof was furnished of any action having taken place.

The slight variations observed may be due to experimental errors, or to the imprisonment or entanglement of the molecules of hydrochloric acid gas amongst the finely powdered particles of Iceland spar, or witherite.

**Dry Acids exert no Action on Litmus and do not form Salts.** — Blue litmus is not changed to red in a stream of dry hydrochloric acid gas. Gore has shown that dry liquefied hydrochloric acid has no action on litmus. Marsh has proved that glacial acetic acid, which is perfectly free from moisture, has no action on litmus. Marsh[1] has also shown that pure sulphuric acid, free from every trace of moisture, does not act on blue litmus, and, further, is probably incapable of forming salts. And Veley[2] has proved that nitric acid, free from moisture and from nitrous acid, is probably incapable of forming salts.

**Dry Hydrochloric Acid does not precipitate Silver Nitrate in Ether or in Benzene.** — Silver nitrate was dissolved in anhydrous ether, and in benzene. A current of dried hydrochloric acid gas was passed through these solutions for an hour. There was no precipitate formed, though the solution became slightly turbid. When the silver nitrate was dissolved in absolute alcohol, a more decided precipitate was formed in the course of an hour, but the decomposition was far from complete. This remarkable result was also obtained by Hughes.

**Comparative Inactivity of Dry Hydrogen Sulphide.** — Veley[3] found that dry hydrogen sulphide does not act on quicklime, and this led Hughes to investigate the action of dry hydrogen sulphide upon metallic oxides.

[1] Chem. News, 61, 2. [2] Phil. Trans. (1891), 279.
[3] Journ. Chem. Soc. (1885), 484; Phil. Mag., 33, 471 (1892).

Magnesium oxide was used. Dry hydrogen sulphide was passed over this, and the increase in weight ascertained. One or two results will show what took place: —

First

| | |
|---|---|
| Weight of magnesium oxide used . . . . . | 0.7597 g. |
| Weight after passing dry hydrogen sulphide . | 0.7600 g. |
| Increase in weight . . . . . | 0.0003 g. |

Second

| | |
|---|---|
| Weight of magnesium oxide used . . . . . | 0.6360 g. |
| Weight after passing dry hydrogen sulphide . | 0.6368 g. |
| Increase in weight . . . . . | 0.0008 g. |

In both cases the increase in weight is within the limit of experimental error. The change from the oxide to the sulphide, which is exothermic and would, therefore, be expected to take place, does not occur.

A drop of water was then added to the magnesium oxide, and dry hydrogen sulphide passed over it as before. The white oxide quickly became greenish yellow, and the following result will show the increase in weight produced.

| | |
|---|---|
| Weight of magnesium oxide and water . . . | 0.7235 g. |
| Weight after passing the hydrogen sulphide gas | 0.8435 g. |
| Gain in weight . . . . . | 0.1200 g. |

The gain in weight, which expresses the amount of oxide transformed into sulphide, is from 200 to 400 times as great as when all moisture is excluded.

Similar results have been obtained with barium oxide.

Dry hydrogen sulphide has no action upon barium oxide, from 15° to 90°.

Ferric oxide showed a slight increase in weight when dry hydrogen sulphide was passed over it. But this was probably due to the incomplete drying of the oxide of iron.

When dry hydrogen sulphide was passed over paper which had been moistened with lead acetate and afterwards thoroughly dried, there was no action whatever. Moist paper containing lead acetate was, of course, acted upon at once. By passing the dried gas first over dry paper, and then over moist, the difference in the action is very striking.

The same experiment was performed, using antimony trichloride instead of lead acetate. The dry paper was unaltered by the dried hydrogen sulphide, while the moist paper was immediately turned yellow. The same experiment was performed with salts of tin, cadmium, bismuth, silver, copper, mercury, and cobalt, and exactly the same results were obtained in all cases.

We may conclude, in general, that dry hydrogen sulphide has no action on the dry soluble salts of the metals, but if moisture is present a change takes place at once.

Hughes[1] found that when mercuric chloride is dissolved in absolute alcohol, a current of dry hydrogen sulphide can be passed for fifteen minutes, without producing any change. Afterwards the solution became slightly turbid, then pale yellow, dark yellow, and finally greenish yellow. No further change took place when the current was passed an hour and a half. The addition of a small amount of water changed the green to a black precipitate.

[1] Phil. Mag., 35, 531 (1893).

**Other Reactions which do not take place without Water.** — According to Baker,[1] sulphur trioxide does not combine with dry lime, or dry copper oxide.

Dry ammonium chloride may be sublimed from a mixture of this salt with dried lime, without ammonia being liberated.

Dry hydrogen and chlorine may be exposed to the sunlight for two days, without anything like complete reaction taking place.

Dry ammonia and hydrochloric acid can be partially separated from a mixture of these gases, when oppositely charged plates are placed in the mixture, the ammonia passing to the negative plate, the hydrochloric acid to the positive.

**Dry Hydrochloric Acid does not act on Dry Ammonia.** — The heading of this paragraph must be a surprise to any one who is familiar with the properties of these gases, and is not acquainted with the experimental work which has been done to establish this fact.

Hughes[2] stated, that when ammonia is dried over lime, and hydrochloric acid is dried by phosphorus pentoxide, the two would remain in the presence of one another for 24 hours, without any deposit being formed, even upon the sides of the containing tube.

H. B. Baker[3] published a very careful investigation of this point, in which the ammonia and hydrochloric acid gases were dried over phosphorus pentoxide, and brought together in such a manner that any change in volume could be readily observed. He concluded, that perfectly dry ammonia and perfectly dry hydrochloric acid gas are entirely without action upon one another.

[1] Journ. Chem. Soc., 65, 611. [2] *Loc. cit.* [3] Journ. Chem. Soc., 65, 611.

The conclusion of Baker was called in question by Gutmann.[1] The latter claimed that ammonia and hydrochloric acid cannot be dried over phosphorus pentoxide, since the gases are absorbed.

Baker,[2] in reply, shows that the phosphorus pentoxide used by Gutmann must have contained metaphosphoric acid. And, further, that Gutmann did not take sufficient care in drying the gases. The glass apparatus must be carefully heated to remove the moisture, which, as is well known, clings to it so tenaciously, and is held by it so persistently. Baker repeated his earlier experiments, working with the greatest care, and found that his original conclusion was confirmed in every respect. Dry hydrochloric acid gas does not combine with dry ammonia gas.

If this fact creates surprise, the following will be almost beyond belief.

**Dry Sulphuric Acid does not act on Dry Metallic Sodium.** — An experiment was performed before the Chemical Society of London,[3] in which a piece of metallic sodium was plunged into concentrated sulphuric acid. When the sodium, wrapped with a piece of wire which served as a handle, was immersed in the acid, there was a flash of light, showing incipient reaction; then there was perfect quiescence, the sodium remaining freely suspended in the sulphuric acid. The reaction at first was due to the presence of a few sodium ions on the surface of the metal, produced by the moisture in the air, to which it was exposed for an instant.

No one should repeat this experiment, unless the greatest

[1] Liebig's Ann., 299, 3. [2] Journ. Chem. Soc. (1898), 422.
[3] Proceed. Chem. Soc. (1894), p. 86.

precautions are taken in drying both the sodium and the sulphuric acid. It is quite evident that ordinary methods of drying would not suffice.

The facts which have been cited in this section show conclusively the necessity of the presence of water in many chemical reactions. The question still remains, why is water essential? We believe we have the answer, in that water has a very high dissociating power, breaking down the molecules into ions, which then react. These facts are just what would be predicted, if the theory of electrolytic dissociation is true.

**Conclusion.** — Some of the lines of evidence bearing upon the theory of electrolytic dissociation have been presented in this chapter. There are many more which might be adduced; but it seems that what has been presented suffices to show how strong the evidence is in favor of the truth of this generalization. It has already been mentioned, and stress should be laid upon it, that there are facts to which the theory, as we now conceive it, does not seem to apply. But the evidence in favor of the theory is so overwhelming, in comparison with the few apparent exceptions, that we should examine the latter very closely before concluding finally that they are real exceptions. Without for a moment ignoring the facts for which the theory does not seem to entirely account, the writer believes that the evidence in favor of a great generalization being expressed by the theory of electrolytic dissociation is as strong as in the case of many of our so-called laws of nature. For how many of these apply under all conditions, and are entirely free from exceptions?

# CHAPTER IV

## SOME APPLICATIONS OF THE THEORY OF ELECTROLYTIC DISSOCIATION

In the last two chapters we have attempted to answer the questions, how did the theory of electrolytic dissociation arise, and what are some of the reasons for believing that it is true? There still remains the question, of what scientific use is this theory? And this brings us to the subject of our last chapter.

Few theories have ever been advanced in science which, in a dozen years, have found wider application than the theory which we are considering. It has already been applied not only to chemical problems, but also to physical, and to biological in the broadest sense. A few of these applications will now be taken up.

### APPLICATION OF THE THEORY OF ELECTROLYTIC DISSOCIATION TO CHEMICAL PROBLEMS

This theory has never directly exercised any marked influence on the study of the relations between the composition and constitution of pure substances, and their properties. This is obviously true, since pure substances are undissociated.

The theory has, however, had an indirect influence in this direction. It has opened up such a number of

entirely new fields of research, that it has detracted from work along these lines. The number of investigations of relations, such as the above, has become less in the last few years; and although an elaborate piece of work has appeared from time to time, the physical chemist of to-day finds more promising lines of work suggested to him by the newer conceptions. Without detracting for a moment from the value of the enormous amount of labor spent in studying the properties of pure substances, yet it should be stated, that the great advances in the last few years have resulted from the study of one substance in the presence of another.

## THE THEORY OF ELECTROLYTIC DISSOCIATION AS APPLIED TO SOLUTIONS

It will be remembered that van't Hoff showed that solutions behave, in certain respects, like gases. There is an analogy between the gas particles distributed in space and the dissolved particles distributed throughout the solvent, — space bearing a similar relation to the gas that the solvent does to the solution. It has also been shown, as stated above, that it is in solutions, chiefly, that we have molecules broken down into ions. Further, the importance of a thorough study of solutions becomes at once apparent, when we consider that most chemical reactions take place in solution. This is especially true of inorganic reactions, most of them taking place in what has come to be known as the wet way. And, indeed, in organic chemistry, also, some solvent is often employed which has the property of dissociating to some extent one or more of the substances present.

We know matter in three states of aggregation, solid, liquid, and gas, and have, therefore, nine classes of solutions: —

| | | |
|---|---|---|
| Gas in gas | Gas in liquid | Gas in solid |
| Liquid in gas | Liquid in liquid | Liquid in solid |
| Solid in gas | Solid in liquid | Solid in solid |

Examples of all of these nine classes are known. We can, however, from the standpoint of the dissociation theory, deal best with solutions in liquids as solvents, and we will, therefore, limit ourselves to solutions of this kind.

**Osmotic Pressure.** — Since van't Hoff[1] pointed out the analogy between the osmotic pressure of dissolved substances and the gas pressure of gases, much work has been done on methods of measuring osmotic pressure. Osmotic pressure, as has already been shown, is a very difficult quantity to measure directly, and a number of comparative methods have been devised. These aim to measure the relative osmotic pressures exerted by different substances. If we, then, know the absolute osmotic pressure of any one of these substances, we can calculate the absolute osmotic pressure of all the others. The relative method of De Vries[2] has already been considered. Those of Tammann,[3] Donders and Hamburger,[4] Wladimiroff,[5] and Löb[6] should be mentioned, in order that they may be examined, if desired. These methods have been applied, not only to non-electrolytes, but also to electro-

[1] *Loc. cit.* [2] *Loc. cit.* [3] Wied. Ann., 34, 299.
[4] Onders Physiol. Lab., Utrecht (3), 9, 26; Ztschr. phys. Chem., 6, 319.
[5] Ztschr. phys. Chem., 7, 529. [6] *Ibid.*, 14, 424.

lytes. Since an ion exerts exactly the same osmotic pressure as a molecule, when we determine the osmotic pressure of a partly dissociated solution, we can calculate the amount to which that solution is dissociated. We know, from the study of non-electrolytes, the osmotic pressure which would be exerted if there was no dissociation; we know that if the electrolytes break down into two ions, that the solution when completely dissociated would give twice this osmotic pressure. Knowing the actual osmotic pressure exerted, we can calculate the amount of dissociation at once. Although we have more accurate methods of measuring dissociation than the above, yet this serves to confirm the results of other methods.

**Diffusion.** — Our knowledge of the osmotic pressure of solutions has thrown light on the way in which salts diffuse in solution. It is well known that a salt always diffuses from the solution into the pure solvent, or from a more concentrated to a more dilute solution; and this continues until the whole has become homogeneous. The law of diffusion was discovered by Fick.[1] "The amount of salt which diffuses through a given cross-section is proportional to the difference in concentrations of two cross-sections lying very close to one another." Diffusion depends, then, upon difference in concentration.

The fundamental question of diffusion is, however, still unanswered. What causes it? What is the force in operation which drives the dissolved substance from one region to another quite remote, if the solution is allowed to come in contact with the pure solvent, or if a more

[1] Pogg. Ann., 94, 59 (1855).

concentrated is brought in contact with a more dilute solution?

We see at once a connection between the law of diffusion and that of osmotic pressure. Diffusion depends upon difference in concentration. Osmotic pressure depends also upon difference in concentration, and a quantitative study of both the diffusion and osmotic pressure of non-electrolytes and electrolytes has shown that osmotic pressure is the cause of diffusion. Wherever there is a difference in the osmotic pressure of two solutions, diffusion will take place from the region of greater into that of less pressure, if the two solutions are brought in contact. This is analogous to the diffusion of gases, which always takes place from the region where the gas exerts a greater pressure to the one where the pressure is smaller.

But there exists a marked difference between the two kinds of diffusion. With gases this takes place very rapidly, and equilibrium is usually established in a short time. But diffusion in solution proceeds very slowly, and it may require weeks and months for a condition of equilibrium to be reached, if the column of liquid has any considerable length.

Nernst[1] has worked out a theory of diffusion based upon osmotic pressure, first for non-electrolytes, which are simpler because there is no dissociation, and then for electrolytes, taking into account their dissociation. This leads to the conclusion, that the forces required to drive dissolved particles through the solvent at any appreciable velocity are enormous. Ostwald[2] has calculated that the force required to drive 60 grams of urea through water,

[1] Ztschr. phys. Chem., 2, 613. [2] Lehrb. allg. Chem., I, p. 697.

with the velocity of 1 cm. per second, has the value of 2500 million kilograms. He suggests that the cause of this is the very fine state of division of the dissolved substance. The force required to throw a small stone with a considerable velocity is not great. But powder the stone very finely, and an enormous force would be required to project the particles of dust with the same velocity. Now let this process of division be continued until the molecules were reached, and forces of the above order of magnitude would be required.

The principle of Soret,[1] which has already been considered, as furnishing evidence for the applicability of the law of Gay Lussac to the osmotic pressure of solutions, should be referred to again in this connection. The change in the concentration of a homogeneous solution, produced by keeping the different parts at different temperatures, has been shown to agree with that calculated from the above law. This principle applies as well to solutions which are dissociated as to those which are not, since an ion exerts the same osmotic pressure as a molecule, and is, therefore, subject to the same law of diffusion.

**Lowering of Freezing-point.** — The theory of electrolytic dissociation has been applied to the lowering of the freezing-point of the solvent produced by the dissolved substance. Reference has already been made to this fact, in connection with the evidence bearing upon the theory. It was there shown that Arrhenius proved that the values of the coefficient "*i*," calculated from freezing-point lowering, agreed with those calculated from conductivity.

[1] *Loc. cit.*, see p. 86.

The freezing-point method was used for a long time, chiefly to determine the molecular weights of substances in solvents which do not dissociate them. The applicability of the freezing-point method to the problem of molecular weights was pointed out by Raoult,[1] several years before the theory of electrolytic dissociation was proposed. By working with solvents other than water, such as formic and acetic acids, benzene, and nitrobenzene, he was able to discover certain general laws of the freezing-point lowering of solvents. When water was used as a solvent, so-called abnormal values were obtained. The freezing-point lowerings were usually much greater than would be expected from what was found in other solvents.

The experimental method used at first by Raoult was necessarily crude, as it had just been devised by him. This has since been very greatly improved by Beckmann.[2] And the method of Beckmann has been enlarged and improved by Jones,[3] Loomis,[4] Lewis,[5] Ponsot,[6] and others. The most refined of all is probably the method described very recently by Raoult,[7] in which he has utilized the best points in all of the above-described methods. However this may be, the freezing-point method has now been developed to a fair degree of perfection.

The direct object in improving the freezing-point method was not the determination of molecular weights, — the method of Beckmann would suffice for this purpose, — but to measure the electrolytic dissociation of acids, bases, and

[1] Ann. Chim. Phys. [6], 2, 66; Harper's Science Series, IV, 71.
[2] Ztschr. phys. Chem., 2, 638, 715; 7, 323.
[3] *Ibid.*, 11, 110, 529; 12, 623; 18, 283.
[4] Wied. Ann., 51, 500; 57, 495; 60, 523.
[5] Ztschr. phys. Chem., 15, 365.
[6] Ann. Chim. Phys. [7], 10, 79.
[7] Ztschr. phys. Chem., 27, 617.

salts in water. There were also certain theoretical questions involved, in connection with the freezing-point constant.

The freezing-point method has already been applied extensively to the measurement of electrolytic dissociation, and is now to be regarded as one of the most general methods for this purpose. The results obtained by Jones, compared with those of Kohlrausch from conductivity, have already been given.

Ions lower the freezing-point of a solvent exactly the same amount as molecules, so that with a partly dissociated electrolyte we have the sum of the lowering of the molecules plus that of the ions. We know, however, from non-electrolytes, how much lowering the molecules alone would produce, and we can calculate from the lowering found, what percentage of the molecules is broken down into ions.

The application of the freezing-point method to the problem of molecular weights in solution has helped to solve a large number of questions, especially in organic chemistry. But from a physical chemical point of view, the newer application of the freezing-point method to the determination of electrolytic dissociation is by far the more important.

**Lowering of Vapor-tension, Rise in Boiling-point.** — What has been said in reference to the lowering of the freezing-point of solvents, can be applied directly to the lowering of their vapor-tension by substances dissolved in them. Here, again, Raoult [1] did much of the pioneer work. The laws of the lowering of vapor-tension, or rise in boiling-

[1] Ann. Chim. Phys. [6], 15, 375; Compt. rend., 104, 1430; Harper's Science Series, IV, 97, 125.

point, had not been discovered, mainly because dissociating solvents had been used. Raoult worked with solutions in ether, and discovered the general law of the lowering of vapor-tension: One molecule of any undissociated substance, dissolved in one hundred molecules of any volatile liquid, lowers the vapor-pressure of this liquid by a nearly constant fraction of its value.

He showed how the lowering of vapor-tension, like the lowering of the freezing-point, can be used to determine the molecular weight of the dissolved substance.

Beckmann[1] improved this method of Raoult, as he had improved the freezing-point method. Instead of measuring the depression of the vapor-tension, he determined the rise in boiling-point, — a quantity which could be much more easily and accurately ascertained. The Beckmann method of determining molecular weights has been modified by a number of investigators. The more important of these improvements are those introduced by Hite,[2] Jones,[3] and Landsberger.[4]

The boiling-point method, like the freezing-point, has been applied also to the measurement of the dissociation of electrolytes. The freezing-point method can be used in this connection, with only a few solvents, since many of the solvents with high dissociating power freeze at a temperature which is too low to deal with successfully in this connection. Indeed, the freezing-point method, as a measure of dissociation, has been applied mainly to aqueous solutions. The boiling-point method for measuring electrolytic

[1] Ztschr. phys. Chem., 4, 532; 6, 437; 8, 223; 15, 656; 17, 107; 18, 473; 21, 239.
[2] Amer. Chem. Journ., 17, 507.
[3] Results will appear in Ztschr. phys. Chem. Jubelband.
[4] Ber. d. chem. Gesell., 31, 458.

dissociation admits of much wider application. It can be employed with formic acid, methyl alcohol, ethyl alcohol, acetone, etc., solvents which have a fairly great dissociating power.

This application of the boiling-point method is of very considerable importance, since it is the only method available for measuring accurately the dissociation of electrolytes in these solvents. The conductivity method cannot give very close results, because of the difficulty of determining the value of the molecular conductivity ($\mu\infty$) at complete dissociation. These solvents all dissociate so much less than water, that, with the exception of formic acid, the dilution at which the dissociation is complete is so great that the conductivity method does not give accurate results. The impurities in the solvents, at these very high dilutions, also render the results imperfect.

The importance of measuring dissociation in solvents other than water will be evident, when we consider that this is the first step toward a physical chemistry in other than aqueous solutions. And, in addition, there is involved a theoretical question of interest and importance. J. J. Thomson [1] has shown, as already mentioned, that if the molecules are held together by the attraction of oppositely charged parts, and if the molecules are broken down into these parts by solvents, the dissociating power of solvents should stand in the same relation as their dielectric constants.

Jones [2] has measured the dissociation of a number of salts in methyl and ethyl alcohol, using his modification

[1] Phil. Mag., 36, 320.

[2] Results will be published in Ztschr. phys. Chem. Jubelband.

of the Beckmann boiling-point apparatus. While he found a qualitative relation between the dielectric constants of these solvents and their dissociating power, compared with water, a proportionality between dielectric constants and dissociating power does not exist, as has already been stated.

The application of the boiling-point method to the problem of electrolytic dissociation has been made only in the last year or two, and much of value will undoubtedly result from further work with this method. It would, doubtless, have been applied much earlier, but for the experimental difficulties involved. The method at first was, of course, imperfect, containing a large number of errors, and, further, the boiling-point constants of solvents are small, and therefore the quantity to be measured was always small. A number of sources of error have now been removed from the boiling-point method, and when all the details are carefully observed, and the entire work carried out with the greatest care and precaution, results can be obtained for the electrolytic dissociation in the alcohols, which should be accurate to within about 1 per cent.

The rise in the boiling-point, like the lowering of the freezing-point, is that produced by both molecules and ions, — an ion lowering the boiling-point to the same extent as a molecule. But in partly dissociated solutions we know, from a study of non-electrolytes, the rise produced by the molecules. We know, further, that if the molecules of the electrolyte were completely broken down into two ions each, the rise in the boiling-point would be twice as great as if there was no dissociation. From the rise

actually found, we can calculate, at once, the percentage of dissociation of the solution in question.

The theory of electrolytic dissociation has been applied to solutions, in a much wider sense than would be inferred from the foregoing. The additive nature of the properties of completely dissociated solutions has already been discussed. It is not necessary to deal, moreover, with solutions of only one electrolyte in a solvent. Two or more electrolytes can be brought simultaneously into the solvent, and the resulting solution studied. The effect of one dissociated substance on another with a common ion has already been indicated. Some interesting properties of solutions, which, when mixed, do not reciprocally affect each other's properties, have been worked out by Arrhenius[1] and others. Arrhenius[2] worked with solutions of acids, and termed those which fulfil this condition, "isohydric." The study of such solutions from the standpoint of his theory, brought out much of interest.

Then, again, we are not limited to one or more electrolytes in one solvent. We can have one or several electrolytes, in one or more solvents; and such cases have been studied. The electrolytes may, or may not, have a common ion, or the solvents may, or may not, be mixable with each other. The number of possibilities is very great, and some have already been studied. But the scope of this work will not allow further detail.

**The Theory of Electrolytic Dissociation as applied to Electrochemistry.** — New light has been thrown upon this entire field, by the theory of electrolytic dissociation. Many facts which were discovered before the theory was

[1] Wied. Ann., 30, 51. [2] Ztschr. phys. Chem., 2, 284.

proposed, have now, by means of it, been correlated, and rationally explained.

**Electrolysis.** — We can now interpret much more clearly the phenomenon of electrolysis. A dilute solution of an electrolyte is completely dissociated; there are no molecules present, all of them having been broken down into ions. When the current is passed through such a solution, it directs the ions, the one to the cathode, the other to the anode, where they give up their charges and separate in the atomic or molecular condition. There appears to be a marked difference between the way in which metallic conductors carry the current, and the manner in which it passes through a solution of an electrolyte. A metal wire carrying a current apparently undergoes no change except in temperature, while a solution conducts only by undergoing simultaneous decomposition, — the positively charged parts moving in one direction, the negatively charged in the other. Although there is apparently such a marked difference in the way in which the two classes of conductors carry the current, a closer study of the two processes brings out relations between them which do not appear on the surface. Indeed, the work of J. J. Thomson has made it probable that there is a close relation between metallic and electrolytic conduction. The view seems to be gaining ground that conduction in metals is also ionic, the ions here being, of course, very much more restricted in their movements.

The ions into which electrolytes dissociate all carry the same amount of electricity, or a simple rational multiple of this unit quantity. This was discovered early in the century by Faraday, and is now the well-known Faraday's

law. All univalent ions carry the same amount of electricity. This we will call the unit. All bivalent ions carry twice, all trivalent ions three times this amount, and so on.

This was proved by the fact, that when a current is passed through solutions of metallic salts containing univalent, bivalent, trivalent, etc., metallic ions, the quantities of the metals which separate stand in the same relations as their chemical equivalents. Univalent metals separate in the ratios of their atomic weights, bivalent in the ratios of one-half their atomic weights, trivalent metals in the ratios of one-third of their atomic weights, and so on.

This connects, directly, the charges carried by the ions with their valence. The combining power of ions is conditioned by the amount of electricity which they carry. If they carry one unit of electricity, they have the smallest valence or combining power. If two units, they have twice the combining power; if three units, three times the power to combine, and so on.

This is exactly what would be expected, if the power to enter into chemical combination was the attraction between oppositely charged parts. The larger the charge carried by the ion, the greater its combining power. We may now say that chemical valence is conditioned by the amount of electricity carried by the ion, and we thus give a more definite and precise meaning to a term which has hitherto been characterized chiefly by vagueness and obscurity.

The law of Faraday, which applies to the amount of electrical energy carried by the ions, has its analogue in

the law of Dulong and Petit, which says, that the capacity for heat energy is the same for all atoms.

After the law of Faraday had been shown to be a true expression of the amount of electricity carried by ions, it became a matter of importance to determine the amount of electricity carried by some unit quantity of ions. The most convenient quantity to use was the atomic weight of the element in grams. The problem, then, was to determine the amount of electricity which would electrolyze a gram-atomic weight of a univalent metal, or half a gram-atomic weight of a bivalent metal. This quantity, termed the "electrochemical equivalent," has been worked out with great care, and with the following result: To separate a gram-atomic weight of a univalent element like silver, requires, in round numbers, 96,540 coulombs of electricity — more accurately 96,537 coulombs. This value is given to show the enormous charges carried by the ions, and also for future reference.

The large amount of electrical energy carried by the ions explains the great difference between the properties of atoms or molecules, and ions. Potassium, sodium, and such substances, when present in the metallic or molecular condition, act upon water with great vigor, while potassium and sodium ions are perfectly inactive toward water. The same distinction applies to a large number of other substances.

The failure to recognize the distinction between atoms or molecules, and ions, that the one is charged and the other not, led to confusion in the early days of the theory of electrolytic dissociation. This distinction, however, has so often been insisted upon, that it is now pretty generally understood.

When electrolytes are decomposed by the current, the ions may give up their charges and separate on the electrodes as metallic ions do, yielding the free metal. Or the ion may be of such a nature that when it loses its charge, and passes over into the atom, or group of atoms, this may act chemically upon the water present, and decompose it. Thus, when a sodium salt is electrolyzed, the sodium ion gives up its charge to the cathode and becomes an atom. But, of course, free sodium cannot exist as such in the presence of water. It decomposes water, forming sodium hydroxide, and hydrogen gas separates from the cathode: —

$$Na + HOH = NaOH + H.$$

This is true of a large number of ions. When they lose their charge, they act upon the water present. When an acid is electrolyzed the hydrogen ion passes to the cathode, gives up its positive charge to this, and escapes as hydrogen gas. The anion, whose nature depends upon the acid used, passes to the anode, and gives up its negative charge (in reality takes up a positive charge). The anion, after it becomes electrically neutral, decomposes the water present. If the acid is hydrochloric, the free chlorine around the anode decomposes water, forming hydrochloric acid, and sets oxygen free: —

$$2\ Cl + H_2O = 2\ HCl + O.$$

When an acid is electrolyzed, we thus have hydrogen set free at one pole and oxygen at the other.

It may be said, in general, that anions, after they have lost their charge, are incapable of existing in the presence

of water, but decompose it chemically, setting oxygen free. A current can, then, be passed through a solution of an electrolyte in only one way. The ions must carry the electricity, and must separate at the electrodes after losing their charge. The cation may separate directly, as the metals do, or it may act upon water, liberating hydrogen. The anion, after losing its charge, usually decomposes water, liberating oxygen at the anode.

The decomposing action of the current has often been used to determine what part of a compound forms the cation, and what part the anion. The principle is simple. The electrolyte is dissolved in water, and the current passed. The cation moves to the cathode, the anion to the anode. After electrolysis, determine what constituents have collected around the two electrodes; that around the cathode is the cation, that around the anode is the anion. In all acids hydrogen is the cation, and the remainder of the molecule, whatever its nature, forms the anion. In the case of some of the organic acids the anion is very complex. The metal in salts forms the cation, the remainder the anion. Bases dissociate into a hydroxyl anion, and the remainder forms the cation. The characteristic ion of acids is hydrogen, of bases is hydroxyl. This same method of determining how a molecule will dissociate has been applied also to very complex cases. How will compounds like $K_4Fe(CN)_6$, $K_2PtCl_6$, $KMnO_4$, dissociate; what will be the cation, and what the anion? This has been determined by electrolyzing solutions of these salts. We would expect that all of the metals would go to the cathode, and the

remainder of the compounds to the anode. These compounds, however, dissociate as follows:—

$$K_4Fe(CN)_6 = \overset{++++}{K_4} + \overset{----}{Fe(CN)_6}.$$

$$K_2Pt(Cl)_6 = \overset{++}{K_2} + \overset{--}{PtCl_6}.$$

$$KMnO_4 = \overset{+}{K} + \overset{-}{MnO_4}.$$

These examples serve to show the relative nature of cation and anion. What is a cation under one condition, may be a part of an anion under other conditions. Take the above cases, iron in iron salts is always the cation, and this applies, also, to platinum and manganese. But in these complex salts, where there is a more positive ion present, such as potassium, these three metals become, respectively, a part of the anion. A number of other cases, similar to these, have been worked out, and many interesting results have been found.

A fact of unusual interest in connection with the charge which ions may carry has been pointed out by Ostwald.[1] An ion having exactly the same chemical composition may carry different charges under different conditions. The ion ($FeCN_6$) may carry four charges, as it does if it comes from the compound $K_4Fe(CN)_6$, or it may have only three charges, if it is a product of the dissociation of $K_3Fe(CN)_6$. Similarly, the ion $MnO_4$ is univalent, if it comes from the compound $KMnO_4$, and bivalent if from $K_2MnO_4$. As Ostwald points out, these are especially interesting cases of isomerism, since it cannot be referred to a different "position of the atoms." The only differ-

[1] Lehrb. allg. Chem., II, p. 588.

ence here is in the charges which the ions carry. The properties of $MnO_4^-$ are very different from $MnO_4^=$. Trivalent iron, manganese, cobalt, etc., have very different properties from bivalent, and there is no more reason to expect them to have the same properties, than to expect that red phosphorus would have the same properties as yellow. In both cases there is a different amount of energy present. This is proved by electrolysis for iron, manganese, etc., compounds. Only two-thirds as much ferric iron will separate for a given current as ferrous, and the same applies to the other compounds. That there are different amounts of energy in the two modifications of phosphorus, is shown by their heats of combustion, which are very different.

The ions with the larger charge usually tend to lose some of it, and pass over into the condition where they carry less electricity. Many of the phenomena which we describe as *oxidation* and *reduction* are due only to the increase and decrease, respectively, of the electrical charges upon the ions,—a ferrous ion passes over into a ferric by taking up one positive charge; a cupric ion becomes a cuprous ion by losing one positive charge.

**Modes of Ion Formation.**—We have spoken of molecules dissociating directly into two, three, and more ions, and have, perhaps, left the impression that electrolytic dissociation can take place in only one way. There are, however, a number of ways in which molecules can break down into ions. The following have been pointed out by Ostwald:[1]—

(1) A molecule may break down directly into an equiva-

[1] Lehrb. allg. Chem., II, p. 786.

lent number of positive and negative ions. This is the case when acids, bases, and salts are dissolved in water. The amount of dissociation depends upon the dilution. Strong acids, strong bases, and salts are completely dissociated in about one one-thousandth normal solutions; while weak acids and bases are completely dissociated only at much greater dilutions.

(2) An electrically neutral substance may take the charge from an ion and become itself an ion, while the original ion, having lost its charge, becomes electrically neutral. The example given by Ostwald is that of one metal displacing another from its salts. When a bar of zinc is immersed in a solution of copper sulphate, the zinc takes the positive charge from the copper, becoming zinc ions, while the copper ions, having lost their charge, separate as metallic copper.

(3) One neutral substance may pass over into positive ions, while another neutral substance may pass over into an equivalent of negative ions. Metallic gold is electrically neutral. Chlorine, when dissolved in water, does not pass over into the ionic condition. But when metallic gold is brought into the presence of chlorine water, the gold passes over into cations, and the chlorine into an equivalent of anions.

It should have been stated earlier, that when gold dissolves in chlorine water auric chloride is formed, and, indeed, this compound is obtained if the solution is evaporated. If the solution is dilute, we have only gold ions and chlorine ions present, and no molecules whatever of gold chloride.

Neither the gold nor the chlorine can pass into ions

when alone, but in the presence of each other they both become ions.

(4) An ion may take up a larger charge than it already carries, converting a neutral substance into an ion with the opposite charge. Thus, a ferrous ion in the presence of chlorine becomes a ferric ion, the chlorine passing from the molecular into the ionic condition. This is an example of a large number of reactions, which are usually termed *processes of oxidation.*

But, on the other hand, an ion may lose a part of the charge which it already carries, converting a neutral substance into an ion of the same electrical character. Thus, when a solution of potassium manganate is treated with chlorine, the $\overset{=}{MnO_4}$ ions, carrying two charges, pass over into the $\overset{-}{MnO_4}$ ions carrying one charge, the negative charge which it has lost going to the chlorine, converting this into an ion. The processes where ions lose part of the charge which they already carry are *processes of reduction.*

These methods of ion formation have all been described by Ostwald,[1] as already stated, and the above examples are those which he has chosen to illustrate the several processes.

**Velocity of Ions.** — Whenever a current is passed through a solution of an electrolyte, there is a mechanical movement of the ions toward the electrodes. To understand the electrochemical behavior of ions, we must study the velocities with which they move through solutions.

If we pass a current through a solution of copper sulphate, using copper electrodes, copper will be deposited

[1] *Loc. cit.*

on the cathode, and exactly an equal amount will pass into solution from the anode. The total amount of copper in solution will thus remain constant, but the color of the solution in the neighborhood of the anode will become deeper, while in the neighborhood of the cathode it gradually becomes less intense. The solution becomes more concentrated in copper around the anode, and less concentrated around the cathode.

If platinum electrodes were used in this experiment, copper would separate at the cathode, and since there is no metallic copper present to pass into solution, the amount in solution would become constantly less. In this case the color would disappear more rapidly around the cathode.

*Relative Velocity of Ions.* — Hittorf[1] was the first to correctly explain this phenomenon. He suggested that it was due to the different velocities with which the anions and cations move. How this explanation can account for the facts, we can see from the following diagram, which we owe in principle to Ostwald.[2]

In the following figure, *I* represents the condition in the solution of the electrolyte before the current has been passed through it. The black circles represent the anions, and the white circles the cations. For each anion present in the solution there is a corresponding cation, and neither anions nor cations have separated at the electrodes.

Let us take a case where the velocity of the anion differs greatly from that of the cation, and for simplicity, let us say that the velocity of the anion is twice as great as

[1] Pogg. Ann., 89, 177; 98, 1; 103, 1; 106, 337, 513. Ueber die Wanderungen der Ionen, Ostwald Klassiker, 21 and 22.

[2] Lehrb. allg. Chem., II, p. 595.

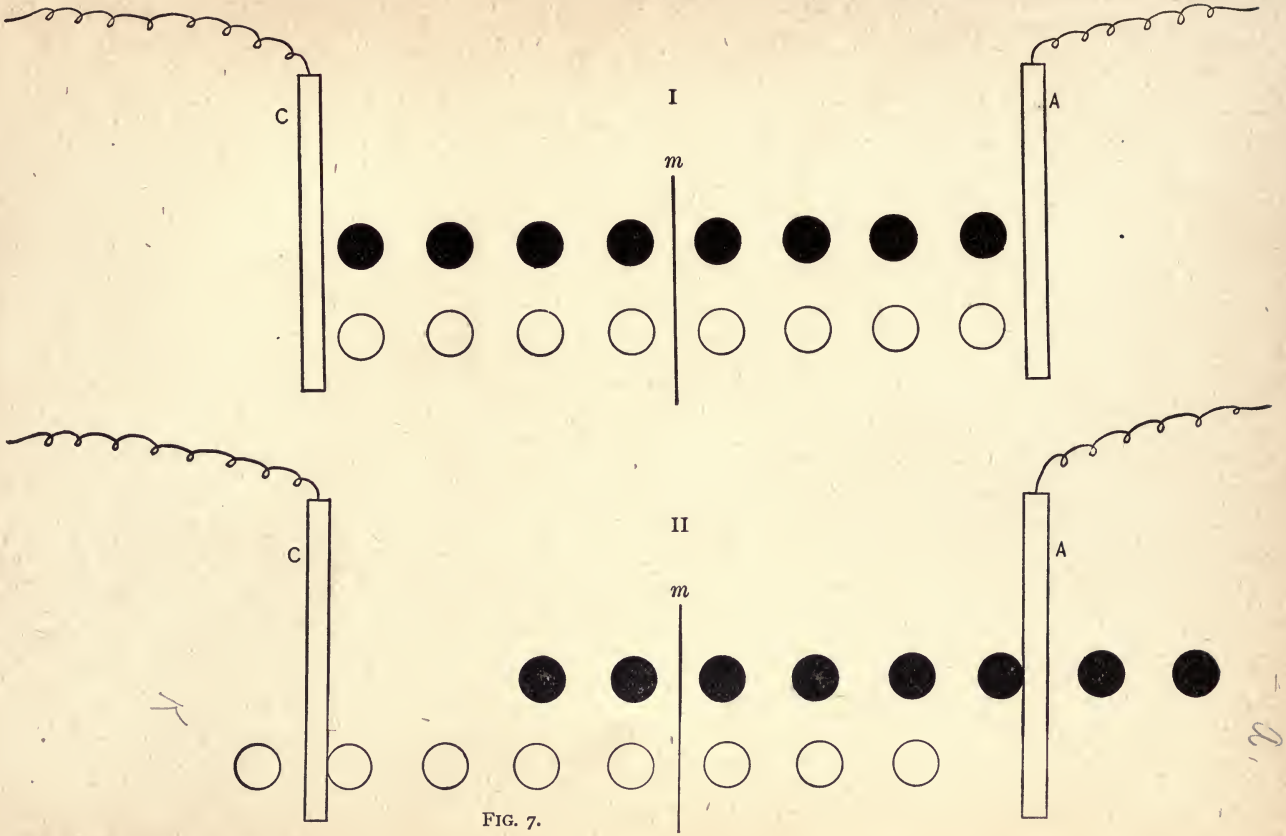


FIG. 7.

that of the cation. Pass a current through the solution until three molecules have been decomposed, and the condition represented in II will exist. Three anions will have separated at the anode, and three cations at the cathode. But the solution will have become, relatively, more concentrated on the anode side of the middle layer marked *m*.

Of the three molecules which have separated from the solution, two have come from the cathode (*C*) side of the middle layer *m*, and one from the anode side (*A*). If we divide the loss around the cathode by the total number of molecules electrolyzed, we will obtain the value $\frac{2}{3}$. If, on the other hand, we divide the loss around the anode by the total number of molecules electrolyzed, the result is $\frac{1}{3}$. But these two values stand to one another in exactly the same relation as the relative velocities of our anion and cation. From this we can make two general statements. First, to find the relative velocity of the cation, divide the loss around the anode by the total amount of electrolyte decomposed. Second, to find the relative velocity of the anion, divide the loss around the cathode by the total amount of electrolyte decomposed.

There are thus three quantities which can be determined experimentally: the change in concentration around the cathode, the change in concentration around the anode, and the total amount of the electrolyte decomposed. It is necessary to determine only two of these, the third being obtained by difference.

The total amount decomposed is, from Faraday's law, proportional to the amount of current passed through the solution; and this is ascertained by measuring the latter by means of a voltameter.

A number of methods, based upon the above principles, have been devised for measuring the relative velocity of ions. The solution must be electrolyzed in part, and the apparatus so constructed that the change in concentration can be measured. To accomplish this, the parts of the solution around the two electrodes must not be allowed to mix after the current is passed, or even while the current is passing.

A number of forms of apparatus were devised, and used, by Hittorf, in which a membrane was interposed to prevent the parts of the solution from mixing again, but it has been found that the membrane affects the results obtained.

Kistiakowsky [1] has devised and used a form of apparatus without any membrane, and thus removed this source of error. Loeb and Nernst [2] have used a form of apparatus which is essentially a Gay Lussac burette. The electrode around which the solution becomes more concentrated is placed below, and the electrolysis is interrupted while there is still an unaltered layer of solution between the two electrodes. This method is not capable of any very high degree of accuracy, since there is no means by which the solutions of different concentrations can be completely separated from one another, removed, and analyzed. The method of blowing out the solution around the anode, together with enough of the unaltered middle layer to wash out the heavier solution, is not in keeping with the most refined work. From work on this problem, which has been carried out in this University, it seems to be far better to measure the amount of current directly, by means

[1] Ztschr. phys. Chem., 6, 97. [2] *Ibid.*, 2, 952.

of a voltameter, than by an indirect method, such as that used by Loeb and Nernst. The work of Bein,[1] on the relative velocity of ions, has extended over a number of years, and very recently an elaborate investigation[2] has been published by him on this problem. The forms of apparatus used by him are modifications of burettes, some of them very elaborate and complex. The work of Bein, taken as a whole, is probably the best which has ever been done on the relative velocity of ions. The objection, however, to the apparatus of Loeb and Nernst, seems to apply here with some force. There does not seem to be any means of completely separating the solutions, after the electrolysis is brought to an end.

At the suggestion of the writer, W. T. Mather,[3] working in this University, undertook to devise a form of apparatus for determining the relative velocity of ions which would be free from the above-mentioned objection.

The form of apparatus which he constructed, and applied successfully in a few cases, consists, essentially, of two upright tubes connected by a U tube, which joins the upright tubes near the top. In the centre of the U tube a stop-cock of large bore is introduced. When the electrolysis has proceeded as far as desired, the stop-cock is closed, and then the solutions in the two arms removed and analyzed. The two parts of the solution are thus completely separated, which is not possible in any form hitherto described.

The methods just described have to do only with the

[1] Wied. Ann., 46, 38.
[2] Ztschr. phys. Chem., 27, 32; 28, 439.
[3] Dissertation, Johns Hopkins University.

relative velocities with which the ions move, and considerable stress has been laid upon this point, because of a generalization which has been reached in connection with these velocities.

*Kohlrausch's Law of the Independent Migration Velocity of Ions.* — F. Kohlrausch[1] carried out a beautiful investigation on the power of solutions of electrolytes to conduct the current, which will be referred to again. The conductivity of a solution, referred to molecular quantities, he termed its "molecular conductivity." He studied the conductivity of solutions at different dilutions, and found that the molecular conductivity increased with the dilution, up to a certain point, and then remained constant, no matter how far the dilution was carried beyond this point. This maximum constant value of the molecular conductivity we will call $\mu_\infty$.

Kohlrausch observed that the difference between the values of $\mu_\infty$, for two electrolytes with a common anion and different cations (say, KCl and NaCl), is the same as the difference when there is another common anion and the same cations as before, thus, $KNO_3$ and $NaNO_3$. This will be seen from the following examples: —

| | | Difference |
|---|---|---|
| KCl | $\mu_\infty = 140$ | 20 |
| NaCl | $\mu_\infty = 120$ | |
| $KNO_3$ | $\mu_\infty = 135.7$ | 22 |
| $NaNO_3$ | $\mu_\infty = 113.7$ | |

[1] Wied. Ann., 26, 160.

Kohlrausch concluded, from a large number of such facts, that the value of $\mu_\infty$ for any electrolyte is the sum of two constants, the one depending upon the anion, the other upon the cation. And these constants are the same for any given ion, regardless of the nature of the other ion which is present in the solution.

These constants are, moreover, the velocities of the anions and cations respectively, and thus Kohlrausch was led to his law of the independent migration velocities of ions.

If we represent the velocity of the cation by $c$, and of the anion by $a$:—

$$\mu_\infty = c + a.$$

From the method of determining the relative velocities, just discussed, we determine the value of $\frac{c}{a}$. Knowing $c + a$ and $\frac{c}{a}$, we can calculate, at once, the values of $c$ and $a$.

*The absolute velocity of ions* can be calculated from the law of Kohlrausch, for a definite fall in potential. The absolute velocity of at least one ion can be determined directly by experiment; and should the calculated value agree with the value found, it would argue very strongly in favor of the law with which we are dealing.

According to Kohlrausch, the absolute velocities of cation and anion ($c$ and $a$ respectively) are obtained from the relative velocities ($c$ and $a$), by multiplying by a factor. For a fall in potential of one volt per centimetre along the tube, or a potential gradient of one volt per centimetre, the value of the factor is $110.10^{-7}$. The absolute velocity of hydrogen, as calculated by Kohlrausch for the above potential gradient, is 0.0032 cm. per second.

The absolute velocity of the hydrogen ion has been measured directly by the beautiful experiment of Lodge.[1]

A glass tube 8 cm. wide and 40 cm. long was carefully graduated. The ends were bent down at right angles. The tube, placed horizontally, was filled with gelatine in which sodium chloride was dissolved. This material was colored red by a little phenolphthaleïn, to which just enough sodium hydroxide had been added to bring out the color. The ends of the glass tube were dipped into vessels filled with dilute sulphuric acid. The apparatus was then allowed to stand, and the rate ascertained at which the acid diffused into the jelly. The current was then passed from one vessel containing the acid, through the horizontal tube, to the other vessel. The hydrogen ions of the sulphuric acid move with the current, displace the sodium ions from the salt, and form hydrochloric acid. This decolorizes the phenolphthaleïn in the jelly, and the movement of the hydrogen ions can thus be traced. When the proper correction is introduced for diffusion, we have at once the velocity of the hydrogen ion for the potential gradient used.

Lodge found, in three experiments, that under a fall of potential of one volt per centimetre, the hydrogen ion has a velocity of 0.0029, 0.0026, and 0.0024 cm. per second. This value agrees very closely with that calculated by Kohlrausch, from his law of the independent migration velocity of ions.

Whetham[2] has measured the absolute velocity of a few ions, using a somewhat different method, which is, however, the same in principle as that of Lodge. The ve-

[1] B. A. Report (1886), 393.

[2] Phil. Trans. (1893), A. p. 337.

locities of the copper ion, and the $Cr_2O_7$ ion, found by Whetham, agree closely with those calculated from the law of Kohlrausch.

It would be difficult to interpret the law of Kohlrausch, if molecules existed as such in very dilute solutions. The law is, however, not only explained by the theory of electrolytic dissociation, but is a necessary consequence of it. In dilute solutions, the molecules are completely broken down into ions, and each of these moves through the solution with a velocity which is definite for a given fall in potential.

The law of Kohlrausch applies to very dilute solutions of strongly dissociated compounds. It holds, at medium dilution, for comparatively few substances, and does not hold at all for the weak acids and bases. How are these facts to be explained?

The theory of electrolytic dissociation furnishes not only an explanation of the law, but an equally satisfactory explanation of the exceptions.

Those solutions to which the law applies are completely dissociated. All of the molecules are completely broken down into ions, and all of the ions take part in conducting the current. The conductivity is, then, a maximum, and gives the true value of $\mu_\infty$. In those cases, however, where the law of Kohlrausch does not apply, the solutions are not completely dissociated. Some of the molecules are not broken down into ions, and these, therefore, take no part in conducting the current. The molecular conductivity of such solutions is not the maximum conductivity — is not the true value of $\mu_\infty$, but is always less. This applies to the fairly concentrated solutions of the most strongly dis-

sociated electrolytes, and even to the very dilute solutions of the weakly dissociated electrolytes, such as the organic acids and bases.

In all such cases, where the solutions are not completely dissociated, we must take into account the amount of the dissociation. When this is done, the law of Kohlrausch becomes much more general, and can be applied, as Ostwald[1] has shown, to partially dissociated solutions.

If we represent the degree of dissociation by $\alpha$, the law becomes: —

$$\mu_\infty = \bar{\alpha}(c + a),$$

which holds for completely dissociated solutions, where $\alpha = 1$, and also for solutions in which the dissociation is not complete.

The relation between the migration velocity of the ions and conductivity is thus completely accounted for by our theory.

**The Conductivity of Solutions.** — The conducting power of a solution is evidently closely connected with its dissociation, since only ions carry the current. We can then obtain new light on the dissociation of solutions by studying their conductivity.

The conductivity of any conductor of electricity is the reciprocal of the resistance of that conductor. The resistance $r$, from Ohm's law, is expressed thus: —

$$r = \frac{\pi}{c},$$

[1] Lehrb. allg. Chem., II, p. 673.

in which $\pi$ is the difference in potential at the two ends of the conductor, and $c$ is the strength of current. The conductivity $C$ is therefore: —

$$C = \frac{c}{\pi}.$$

The unit of resistance most generally used is that of a column of pure mercury 106 cm. in length and 1 sq. mm. in section, at 0° C. (Ohm)

*Specific Conductivity.* — The resistance of conductors depends upon their form as well as upon their chemical nature. In order, therefore, that the resistances of different substances may be measured so as to be comparable, it is necessary that the conductors should have the same or comparable forms. The dimensions usually chosen are a cylinder 1 m. in length and 1 sq. mm. in section. The resistance offered by substances of these dimensions is known as their specific resistance.

The term "specific resistance" is, sometimes, applied also to the resistance offered by a cube whose edge is 1 cm. in length. This is $\frac{1}{10000}$ of the former.

The term "specific resistance," or its reciprocal, "specific conductivity," can be applied to conductors of the second as well as to those of the first class. In this case, the specific conductivity would be the conductivity of a cylinder of the liquid 1 m. in length and 1 sq. mm. in cross-section.

Conductors of the second class are, however, generally solutions of some electrolyte in some solvent, and their conductivity is conditioned by the presence of the electrolyte. That the resistances of such solutions should be comparable, it is clear that we must deal with comparable

quantities of the dissolved substances. The most convenient quantities are gram-molecular weights of the different substances.

Given a normal solution, which contains a gram-molecular weight of the electrolyte in a litre. Let us place the litre of solution between two electrodes which are 1 cm. apart. The cross-section of this solution would be 1000 sq. cm.

If we represent by $v$ the number of cubic centimetres of any solution which contains a gram-molecular weight of the dissolved substance, and by $s$ the specific conductivity of a cube of the solution whose edge is 1 cm. in length, the *molecular conductivity*, $\mu$, is the product of these two: —

$$\mu = vs.$$

But if we represent by $s$ the specific conductivity of a prism of the solution, 1 m. in length and 1 sq. mm. in cross-section, the molecular conductivity is expressed thus: —

$$\mu = 10000\, vs.$$

A general expression for the molecular conductivity, where $g$ gram-molecular weights are contained in a litre of the solution, is: —

$$\mu = \frac{s \times 10^3}{g} \text{ or } \mu = \frac{s \times 10^7}{g},$$

depending upon our definition of specific resistance, whether it is referred to a cube of the solution whose edge is 1 cm. long, or to a cylinder of it 1 m. long and 1 sq. mm. in cross-section.

*Method of Measuring the Conductivity of Solutions.* — If a continuous current is passed through an aqueous solution of an electrolyte from, say, platinum electrodes,

the electrodes will become covered with gas. The resistance of the solution cannot then be measured as such, since this polarization of the electrodes will introduce a new source of resistance into the circuit. The effect of polarization must be overcome by some means. Kohlrausch has accomplished this by using an alternating current. His method consists in passing an alternating current from a very small induction coil between platinum

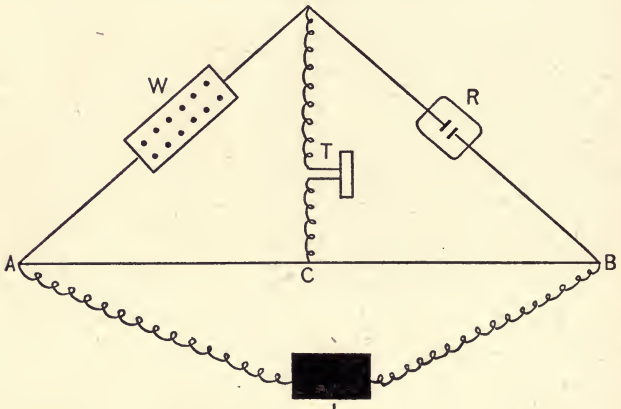


FIG. 8.

plates immersed in the solution. The resistance of the solution is balanced against a rheostat, using a Wheatstone bridge and telephone. A dynamometer may be used instead of the telephone, for determining the reading on the bridge. A galvanometer cannot, of course, be used with an alternating current.

The Kohlrausch apparatus is sketched diagrammatically in Fig. 8. *J* is a small induction coil, tuned to a very high pitch, and should be placed at some distance from the

bridge, or enclosed in a box lined with cotton, to deaden the sound. It is driven by a storage cell. $AB$ is a metre stick divided accurately into millimetres. Over this is stretched a wire of platinum, or, better, of manganine (an alloy containing manganese) or nickelic, which have a very small temperature coefficient of resistance. $W$ is a rheostat. $R$ is the vessel containing the solution and electrodes. The electrodes are cut from thick sheet platinum, and into each plate a piece of stout platinum wire, about an inch in length, is welded. The wire is sealed into a glass tube which is filled with mercury, and electrical connection thus established between the plate and the copper wire which is immersed in the mercury. One arm of the telephone $T$ is thrown into the circuit between the rheostat and the resistance vessel, and the other arm is connected with the bridge wire by means of a slider. This is moved along the wire until that point is found at which the hum of the induction coil ceases to be audible in the telephone. If this is some point $C$, and we represent $AC$ by $a$, $BC$ by $b$, the resistance in $W$ by $w$, and the resistance of the solution in the vessel by $r$, then from the principle of the bridge we have: —

$$ra = wb,$$

$$r = \frac{wb}{a}.$$

But the conductivity of a solution $c$ is the reciprocal of the resistance $r$; therefore: —

$$c = \frac{a}{wb}.$$

The conductivities of solutions determined from this expression would not be comparable with one another,

since there is nothing in this expression which takes into account the concentration of the solution. It is most convenient to refer all concentrations to molecular normal, which contains a gram-molecular weight of the electrolyte in a litre. If we represent by $v$ the number of litres of the solution which contains a gram-molecular weight of the electrolyte, the above expression becomes: —

$$c = \frac{va}{wb}.$$

Instead of $c$, we now write for the molecular conductivity the letter $\mu$. And to indicate the concentration at which the $\mu$ is determined, we write $\mu_v$.

$$\mu_v = \frac{va}{wb}.$$

Even this expression does not take into account the dimensions of the cell used. A cell constant $k$ must be introduced and determined for each cell, before it can be employed for conductivity measurements. The complete expression for calculating the molecular conductivity $\mu_v$ is then: —

$$\mu_v = k\frac{va}{wb}.$$

**Carrying out a Conductivity Measurement.** — To carry out a conductivity measurement, the constant $k$ for the cell must first be determined. For this purpose a solution must be used whose value of $\mu_v$ is known. The value of $\mu_v$ for a one-fiftieth normal solution of potassium chloride at 25° is 129.7.

The platinum plates are covered with platinum black, by electrolyzing, in the cell, a dilute solution of platinic

chloride. The $\frac{n}{50}$ solution of potassium chloride is placed in the cell, the latter introduced into a thermostat which is exactly at 25°, and the values of $a$, $b$, and $w$ ascertained; $v$ and $\mu_v$ are known, and $k$ can be calculated at once.

Having determined the cell constant, the measurement of the conductivity of a solution is comparatively simple. The solution of known concentration is placed in the cell, warmed accurately to the temperature desired, and then the values of $a$, $b$, and $w$ ascertained; $k$ and $v$ being known, $\mu_v$ is calculated at once.

**Conductivity of Water.** — The conductivity of the water used is very important. When we determine the conductivity of an aqueous solution, what we actually measure is the sum of the conductivities of the electrolyte and of the water used in preparing the solution. For this reason very pure water must be used in such work, and a number of methods for purifying water for conductivity measurements have been devised.

It is quite certain that perfectly pure water has never been prepared. The purest has undoubtedly been obtained by Kohlrausch and Heydweiller.[1] They distilled in a vacuum the purest water obtainable by other methods, and determined its conductivity without allowing it to come in contact with the air. A millimetre of this water, at zero degrees, has a resistance equal to that of a copper wire 1 mm. in diameter, extending one thousand times around the earth.

It is, of course, not practicable to prepare water of this degree of purity for ordinary conductivity measurements.

[1] Ztschr. phys. Chem., 14, 317.

A number of methods are, however, available for purifying water sufficiently for such measurements.

Nernst[1] suggests fractional crystallization. Hulett[2] distilled water first from potassium bichromate and sulphuric acid, and then redistilled it from a solution of barium hydroxide.

Jones and Mackay[3] distilled ordinary distilled water from potassium bichromate and sulphuric acid, and then passed the vapor directly into a boiling alkaline solution of potassium permanganate. Two distillations were thus effected at once.

Any of the above methods will yield water of sufficient purity for ordinary conductivity work.

The fact that pure water does not conduct the current, means that it is practically undissociated. This same fact has been shown by a number of independent investigations, in which widely different methods have been used. Space will not permit of a discussion of these exceedingly interesting pieces of work. Reference only can be made to that of Wijs,[4] Arrhenius,[5] Ostwald,[6] Bredig,[7] Nernst,[8] and Kohlrausch.[9] The reader is urgently advised to carefully examine these investigations, which all agree in showing that water is very slightly dissociated.

The fact that water is undissociated is of great importance. It means that hydrogen and hydroxyl ions cannot remain in the presence of each other uncombined. This has already been referred to (p. 122), in connection

[1] Ztschr. phys. Chem., 8, 120.
[2] *Ibid.*, 21, 297.
[3] *Ibid.*, 22, 237; Amer. Chem. Journ., 19, 91.
[4] *Ibid.*, 11, 492.
[5] *Ibid.*, 5, 16.
[6] *Ibid.*, 11, 521.
[7] *Ibid.*, 11, 829.
[8] *Ibid.*, 14, 155.
[9] *Ibid.*, 14, 317.

with the explanation of the phenomenon of neutralization of acids and bases. The great tendency of hydrogen and hydroxyl ions to unite is, undoubtedly, the conditioning cause of a large number of chemical reactions. This will become apparent, when we recall how many chemical reactions there are in which a molecule of water is formed.

**Calculation of Dissociation.** — The calculation of dissociation from conductivity is comparatively simple. The molecular conductivity of strong acids and bases and salts increases from any moderate dilution up to a dilution of about 1000 litres, where it becomes constant. This maximum constant value of the molecular conductivity means complete dissociation. If the solution is not dissociated at all, the conductivity, and, consequently, the molecular conductivity, is zero. To calculate the dissociation of any partially dissociated solution, it is only necessary to determine the ratio between the molecular conductivity of the solution in question and the molecular conductivity of the substance when completely dissociated.

Representing the molecular conductivity of the solution of volume $v$ by $\mu_v$, and the molecular conductivity when the substance is completely dissociated by $\mu_\infty$, the percentage of dissociation $\alpha$ is calculated thus: —

$$\alpha = \frac{\mu_v}{\mu_\infty}.$$

The value of $\mu_v$ for any dilution of any substance can be ascertained at once by means of the conductivity method. The value of $\mu_\infty$ for the strongly dissociated electrolytes can also be determined directly by the conductivity method. It is only necessary to increase the

dilution of the solution until the molecular conductivity attains a constant maximum value. This is usually reached at about 1000 litres. If the electrolyte is not strongly dissociated, as in the case of the organic acids and bases, resort must be had to an indirect method of determining the value of $\mu_\infty$. This, again, can only be referred to,[1] since space will not allow it to be more fully discussed.

It will be seen at once from Kohlrausch's law, that the conductivity method can also be used to determine the *velocity* of *ions*. In terms of this law the value of $\mu_\infty$, for any compound, is the sum of two constants, the one depending upon the anion, and the other upon the cation. These constants represent, further, the relative velocities of the two ions.

Given a compound like hydrochloric acid; we determine the value of $\mu_\infty$ for the compound, by the conductivity method. This is the sum of the velocities of the hydrogen and chlorine ions. We know the velocity of the hydrogen ion. If we subtract this from the value of $\mu_\infty$ for hydrochloric acid, we obtain the velocity of the chlorine ion.

This principle has been used extensively, especially by Ostwald[2] and Bredig,[3] for determining the relative velocity of ions. The work of Ostwald is typical. He wished to determine the relative velocities of the anions of a number of organic acids. He prepared the sodium salts of each of these acids, and determined the value of $\mu_\infty$ for these sodium salts, by the conductivity method. The value of $\mu_\infty$ for the sodium salts is, from Kohlrausch's

[1] Ostwald, Lehrb. d. allg. Chem., II, p. 692.
[2] Ztschr. phys. Chem., 2, 840. [3] *Ibid.*

law, the sum of the velocities of the sodium cation and of the organic anion of the acid. Knowing the velocity of sodium to be 44.5 in terms of the units used, he had but to subtract this number from the $\mu_\infty$ for the acid, to obtain the velocity of the anion of the acid.

Bredig[1] worked on a very large number of organic bases. Here, it was necessary to prepare a salt of the base which would be strongly dissociated, and would give the value of $\mu_\infty$ at moderate dilutions. If the hydrochloric acid salt was used, the velocity of chlorine must be subtracted from the $\mu_\infty$ found, and the difference would be the velocity of the organic cation.

It is thus a very simple matter to determine the relative velocities of cations and anions, since Kohlrausch discovered the law to which these conform.

A number of stöichiometric relations between the composition and constitution of ions, and their velocities, have been pointed out by Ostwald and Bredig. In general, the more complex the ion the slower it moves. Isomeric anions have very nearly the same velocity, while constitution has a marked influence on the velocity of cations. The effect of certain atoms, and also of the symmetry of the molecule, have been worked out by Bredig.[2] For details in this connection, his original communication must be consulted.

*The conductivity of solutions in the different solvents varies very greatly.* Solutions in water were thought to have the greatest conductivity, until it was recently shown that solutions in liquid ammonia conduct better than in water. This fact has been confirmed by Goodwin

[1] *Loc. cit.* [2] *Loc. cit.*

and Thompson, in their work on the dielectric constant of liquid ammonia. Next to these solvents, in dissociating power, come formic acid, methyl alcohol, ethyl alcohol, acetone, and finally the oils, hydrocarbons, and ethereal salts. When substances which conduct well in water are dissolved in the last-named solvents, the solutions, as has already been mentioned, show very little conductivity, and are, therefore, very slightly dissociated.

The dissociation in solvents whose solutions conduct but little cannot be measured accurately by the conductivity method, on account of the difficulty of determining the value of $\mu_\infty$. The most strongly dissociated electrolytes are not completely dissociated by these solvents, at dilutions which come within the range of the conductivity method. Thus, it is impossible to determine the value of $\mu_\infty$ for any substance in ethyl alcohol, by the conductivity method. The values of $\mu_v$, for any dilution, can be determined in these solvents as well as in water. Some assumption, however, must be made in calculating the value of $\mu_\infty$, which may introduce considerable error.

The freezing-point method can be used with only a few solvents, because most substances freeze at temperatures which are too far removed from the ordinary to secure accurate measurements.

The boiling-point method is, at least theoretically, the freest from objections in such cases, and could be used to measure dissociation, if the experimental difficulties could be overcome.

This has been accomplished, in part, by H. C. Jones.[1] He has devised a boiling-point apparatus which diminishes

[1] Amer. Chem. Journ., 19, 581.

some of the sources of error inherent in other forms, and he has applied this to the measurement of electrolytic dissociation in methyl and ethyl alcohols.[1] The results obtained are fairly satisfactory. A comparison of the dissociation of a few salts, by water, methyl alcohol, and ethyl alcohol, taken from the paper of Jones, is given in the following table:—

| Substance | Dilution Normal | Dissociation in Water | Dissociation in Methyl Alcohol | Dissociation in Ethyl Alcohol |
|---|---|---|---|---|
| KI, | 0.1 | 88% | 52% | 25% |
| NaI, | 0.1 | 84% | 60% | 33% |
| $NH_4I$, | 0.1 | | 50% | |
| KBr, | 0.1 | 86% | 50% | |
| NaBr, | 0.1 | 86% | 60% | 24% |
| $NH_4Br$, | 0.2 | | 49% | 21% |
| $CH_3COOK$, | 0.1 | 83% | 36% | 16% |
| $CH_3COONa$, | 0.1 | | 38% | 14% |

The dissociation in methyl alcohol is more than half of that in water. The dissociation in ethyl alcohol is less than one-third of that in water.

This method can also be applied to the investigation of solutions in other solvents.

**Thomson's Theory.** — Reference has already been made to a theory proposed by J. J. Thomson,[2] which connects the dissociating power of solvents with their dielectric constants. This theory will now be given, in Thomson's own words. "If we take the view that the forces which hold the atoms in the molecules together are electrical in their origin, it is evident that these forces will be very much diminished when the molecule is close to the surface of, or

[1] Ztschr. phys. Chem., Jubelband, van't Hoff.
[2] Phil. Mag., 36, 320.

surrounded by, a conductor, or a substance like water, possessing a very large specific inductive capacity (dielectric constant).

"Thus, let $A$, $B$ represent two atoms in a molecule, placed near a conducting sphere, then the effect of the electricity induced on the sphere by $A$ will be represented by an opposite charge placed at $A'$, the image of $A$ in the sphere. If $A$ is very near the surface of the sphere, then the negative charge at $A'$ will be very nearly equal to that at $A$. Thus, the effect of the sphere will be practically to neutralize the electric effects of $A$; as one of these effects is to hold the atom $B$ in combination, the affinity between the atoms $A$ and $B$ will be almost annulled by the presence of the sphere. Molecules condensed on the surface of the sphere will thus be practically dissociated.

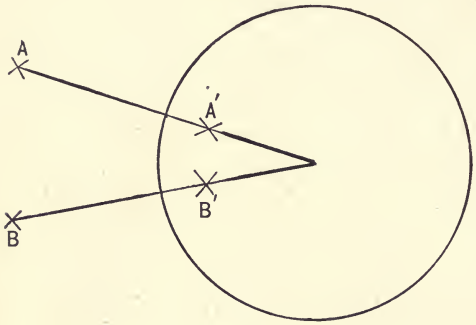

FIG. 9.

"The same effect would be produced, if the molecules were surrounded by a substance possessing a very large specific inductive capacity. Since water is such a substance, it follows, if we accept the view that the forces between the atoms are electrical in their origin, that when the molecules of a substance are in aqueous solution, the forces between them are very much less than they are when the molecule is free, and in a gaseous state."

The above results show that the solvent with the higher dielectric constant has the higher dissociating power, but that the two are not proportional is seen by comparing the above values for dissociation, with the dielectric constants of these three solvents.

| | Dielectric Constant |
|---|---|
| Water, | 76 to 78 |
| Methyl alcohol, | 32.5 to 34 |
| Ethyl alcohol, | 25.7 to 26 |

We have not yet sufficient data to fairly test the value of Thomson's theory. It is so beautiful and simple, and is such a welcome application of the theory of electrolytic dissociation, that we are inclined to hope that it may be of wide-reaching significance.

**Conductivity at Elevated Temperatures.** — We have, thus far, dealt with the conductivity of solutions — of one substance in the presence of another. The question still remains: Do any substances conduct by undergoing decomposition when alone? Pure substances conduct without undergoing decomposition, such as the metals, carbon, etc., which belong to conductors of the first class. But substances which undergo decomposition when they conduct are called conductors of the second class. Do any pure homogeneous substances belong to the second class?

At elevated temperatures, a number of pure substances are known to conduct like conductors of the second class, or electrolytes. Substances which are liquid at ordinary temperatures do not conduct, and are, therefore, non-electrolytes.

It thus seems that heat acts, to a certain extent, like

a solvent, converting a substance which does not conduct into one which has the power to carry the current.

**Electromotive Force.** — The theory of electrolytic dissociation has also been applied, with beautiful results, to the problem of the source of the electromotive force in primary cells. This could properly be dealt with under the head of electrochemistry, but is so distinctly physical in its nature, that it will be taken up as an example of the application of this theory to physical problems.

**Strength of Acids and Bases.** — The applications of the theory of electrolytic dissociation, described in this section, we owe almost entirely to Ostwald. Reference has already been made to his extensive investigations of the conducting power of electrolytes, and especially of the organic acids. His law connecting dissociation with dilution has already been deduced. It will be remembered that, if we represent the percentage of dissociation by $\alpha$, and the dilution of the solution, or number of litres which contains a gram-molecular weight of the electrolyte, by $v$, the Ostwald dilution law is:

$$\frac{\alpha^2}{(1-\alpha)v} = \text{constant.}$$

It has already been pointed out, that this law does not hold for the strongly dissociated electrolytes, the strong acids and bases, and the salts; but does apply to the more weakly dissociated compounds, such as the organic acids and bases.

Ostwald has shown that the value of the constant for a substance is a characteristic of that substance, and an expression of its chemical activity.

The constant for any substance is determined by measuring the conductivity of the substance at several dilutions, calculating the dissociation from these measurements, by means of the formula $\alpha = \frac{\mu_v}{\mu^\infty}$, already considered; and knowing $\alpha$ and $v$, the constant $c$ is calculated from the Ostwald dilution law, just given. An example, taken from the work of Ostwald,[1] will make this clear.

FORMIC ACID (HCOOH). $\mu_\infty = 376$

| $v$ | $\mu_v$ | $\alpha$ | $c \times 100$ |
|---|---|---|---|
| 8 | 15.22 | 4.05 | 0.0214 |
| 16 | 21.19 | 6.63 | 0.0210 |
| 32 | 29.31 | 7.79 | 0.0206 |
| 64 | 40.50 | 10.78 | 0.0203 |
| 128 | 55.54 | 14.76 | 0.0200 |
| 256 | 75.66 | 20.12 | 0.0198 |
| 512 | 102.1 | 27.10 | 0.0197 |
| 1024 | 134.7 | 35.80 | 0.0195 |

The constants of other acids and bases were determined in exactly the same manner. In this investigation, Ostwald studied between two and three hundred organic acids, and brought out some interesting and important facts in connection with the strength of these acids, and pointed out certain relations between the strength of the acids and their composition and constitution.

In the preceding chapter, it was shown that the strength of acids thus determined by conductivity, agreed with that found by other methods, such as the velocity with which they inverted cane-sugar, saponified methyl acetate,

[1] Ztschr. phys. Chem., 3, 170, 241, 369.

etc. We can, then, regard conductivity as the true measure of the strength of acids.

But conductivity is proportional to dissociation, since only ions conduct the current. Therefore, the strength of an acid is conditioned by the amount to which it is dissociated.

All acids dissociate into a hydrogen cation, and into the remainder of the molecule which forms the anion. The anion may be simple, consisting of the halogen alone, as with the halogen acids, or it may be very complex, as with the higher members of the homologous series of organic acids. The anion differs in its nature with every acid. The cation of all acids, however, is hydrogen, and, therefore, the acidity of these compounds is due to this common constituent into which all acids dissociate.

The strength of acids, then, resolves itself into the number of hydrogen ions present in their solutions. When we say an acid is strong, we mean that it is largely dissociated in solution, or that its solution contains a large number of hydrogen ions. And this leads us to an interesting conclusion pointed out by Ostwald. All acids are completely dissociated at infinite dilution; therefore, at infinite dilution all acids have the same strength. Exactly the same remarks apply to bases. Bases dissociate into a hydroxyl anion, and the remainder of the compound forms the cation. The latter may be simple, as with the alkalies, or may be very complex, as in the organic bases.

The common constituent of bases is, then, the hydroxyl anion, and basicity is due to the presence of this ion. A strong base means one which is largely dissociated, or in whose solution there is a large number of hydroxyl ions. But all bases, like all acids, are completely disso-

ciated at infinite dilution. Therefore, all bases have the same strength at infinite dilution.

These generalizations for acids and bases are of very wide significance, and greatly simplify and correlate phenomena, which have been hitherto regarded as more or less disconnected.

**Relations between Acidity and Composition and Constitution.** — Some of the relations between acidity and composition and constitution will be considered.

Hydrochloric, hydrobromic, and hydriodic acids are to be ranked among the strongest acids. They have very nearly the same strength, as is shown by the fact that they conduct to just about the same extent. Hydrofluoric acid is much weaker, as is shown by its comparatively small conductivity. These facts are established by the following results: —

| | HCl | HBr | HI | HF |
|---|---|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ |
| 2 | 331 | 341 | 341 | — |
| 4 | 343 | 354 | 353 | 27.8 |
| 8 | 355 | 361 | 360 | 33.6 |
| 32 | 369 | 373 | 372 | 55.8 |
| 4096 | 376 | 372 | 373 | — |

Hydrocyanic acid conducts but little better than pure water, and is, therefore, one of the weakest acids. When sulphur is introduced into this acid, we have, in sulphocyanic, one of the strongest acids.

| | HCN | HCNS |
|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ |
| 2 | — | 326 |
| 4 | 0.33 | 337 |
| 8 | 0.38 | — |
| 32 | 0.46 | 358 |

Hydrocyanic acid, judged by its conductivity, can, therefore, scarcely be regarded as an acid, while sulphocyanic acid is nearly as strong as hydrochloric acid.

The introduction of oxygen usually increases the acidity, that is to say, forms a compound which is more dissociated by the solvent. This is by no means general. Take the acids of phosphorus; the more oxygen there is present the weaker the acid, as is seen in the following results: —

| | $H_3PO_2$ | $H_2PO_3$ | $H_3PO_4$ |
|---|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ |
| 2 | 131 | 121 | 60 |
| 8 | 194 | 175 | 90 |
| 64 | 293 | 274 | 183 |
| 256 | 330 | 316 | 262 |
| 1024 | 344 | 336 | 320 |

The order of strength of some of the more common mineral acids is as follows, expressed in terms of hydrochloric acid = 100: —

| | | | |
|---|---|---|---|
| HCl | 100 | HBr | 101 |
| $HNO_3$ | 99.6 | HI | 92 |
| $H_2SO_4$ | 65.1 | $H_3PO_4$ | 17 |

Turning to the organic acids, we find a number of relations established. The introduction of chlorine into the fatty acids increases the acidity. Take the chlorine substitution products of acetic acid: —

| | $CH_3COOH$ | $CH_2ClCOOH$ | $CHCl_2COOH$ | $CCl_3COOH$ |
|---|---|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ |
| 2 | — | 21.2 | 109 | 245 |
| 32 | 8.65 | 73.4 | 256 | 327 |
| 128 | 16.99 | 126.0 | 308 | 336 |
| 1024 | 46.00 | 236.0 | 342 | 339 |

The introduction of oxygen into an acid, forming the hydroxyl group, increases the acidity. This is seen from the following example:—

| | Succinic Acid $C_2H_4(COOH)_2$ | Malic Acid $C_2H_3(OH)(COOH)_2$ | Tartaric Acid $C_2H_2(OH)_2(COOH)_2$ |
|---|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ |
| 2 | 3·73 | 8.45 | — |
| 32 | 15.7 | 26.6 | 58.1 |
| 64 | 22.1 | 50.8 | 79.4 |
| 512 | 58.6 | 126.0 | 183.0 |
| 4096 | 142.0 | 255.0 | 341.0 |

The effect of introducing one and two hydroxyl groups is shown in these examples.

In the *aromatic series* we have to take into account not simply the nature of the group, but the position which it takes, whether ortho, meta, or para. The introduction of oxygen into benzoic acid, forming a hydroxy acid, has a very different influence on the acidity, depending upon the position occupied by the oxygen.

| | Benzoic Acid | Salicylic Acid (o) | *M*-Oxybenzoic Acid | *P*-Oxybenzoic Acid |
|---|---|---|---|---|
| | $C_6H_5COOH$ | $C_6H_4(OH)COOH$ | $C_6H_4(OH)COOH$ | $C_6H_4(OH)COOH$ |
| $v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ |
| 64 | 22.1 | 81.2 | 25.5 | 14.3 |
| 256 | 42.3 | 137.0 | 47.7 | 28.3 |
| 2048 | 104.0 | 255.0 | 114.0 | 73.0 |

Hydroxyl in the ortho position increases the acidity very markedly. In the meta position it has but a slight effect, while in the para position it actually lessens the acidity.

The introduction of the nitro group has a very different influence, depending upon its position.

| | Benzoic Acid | *O*-Nitrobenzoic Acid | *M*-Nitrobenzoic Acid | *P*-Nitrobenzoic Acid |
|---|---|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ |
| 64 | 22.1 | 159 | 47.5 | — |
| 512 | 57.9 | 263 | 117.0 | 123 |
| 2048 | 104.0 | 301 | 190.0 | 195 |

The nitro group in the ortho position has the greatest acidifying power, while in the para position it has somewhat greater power than in the meta.

The introduction of more and more nitro groups, in general, increases the acidity. Thus, take phenol, which is a very weak acid. Introduce one nitro group, we have its acidity increased. Introduce a second nitro group, and its acidity is still further increased. Introduce the third nitro group, and we have picric acid, which is nearly as strong as the mineral acids.

As the *unsaturated acids* contain less and less hydrogen, the affinity increases. Thus, acrylic acid, $C_3H_4O_2$, is stronger than propionic, $C_3H_6O_2$. The effect of constitution can be seen by studying the acidity of maleïc and fumaric acids, which have the same composition.

| | Maleïc Acid | Fumaric Acid |
|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ |
| 32 | 166 | 58.8 |
| 512 | 305 | 179.0 |
| 2048 | 338 | 275.0 |
| 8192 | 339 | 337.0 |

Maleïc is much stronger for the greater concentrations, but never has a molecular conductivity greater than a monobasic acid. Fumaric, at high dilution, has a greater conductivity than a monobasic acid. The second hydro-

gen takes part in the conductivity, before the first has reached a maximum.

Take citraconic acid and two of its isomeres:—

| | Citraconic | Itaconic | Mesaconic |
|---|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ |
| 8 | 56.4 | 11.7 | 25.5 |
| 512 | 250.0 | 84.7 | 162.0 |
| 4096 | 322.0 | 186.0 | 291.0 |

From its conductivity, citraconic acts like a monobasic acid. In itaconic one carboxyl is weaker than the other, while mesaconic conducts itself like a dibasic acid, whose hydrogen atoms are nearly or quite equivalent. By a careful study of the conductivity of acids, as Ostwald has shown, some light can be thrown on their constitution.

The introduction of the amido group weakens the acid properties, as would be expected from the basic nature of this group.

**Bases.** — Some work has been done on strength of bases by Ostwald,[1] Bredig,[2] and others. But these have not been worked up as thoroughly as the organic acids.

The conductivities of the strong bases, like those of the strong acids, reach a maximum at a dilution of about one thousand litres. The value of $\mu_\infty$ for the bases is less than for the acids, since the velocity of the hydroxyl ion is only about 170, while the velocity of the hydrogen ion is about 325 at 25°C. The strong bases include the hydroxides of the alkalies and alkaline earths. Ammonia is sometimes regarded as a strong base, but it is not.

[1] Journ. prakt. Chem. (2), 33, 352.
[2] Ztchr. phys. Chem., 13, 289.

It was found that the conductivity of ammonia is slight, compared with that of, say, potassium hydroxide. Other reactions with ammonia were also studied, such as the velocity with which it would effect reactions, and these results confirmed those from conductivity. Ammonia is, then, a comparatively weak base.

We will now compare the strength of ammonia with that of the substituted ammonias:—

| | $NH_3$ | $NH_2CH_3$ | $NH_2C_2H_5$ | $NH_2C_3H_7$ | $NH_2C_4H_9$ |
|---|---|---|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ |
| 2 | 1.46 | 6.41 | 6.06 | — | — |
| 32 | 6.13 | 26.4 | 26.8 | 23.7 | 19.5 |
| 256 | 17.8 | 64.8 | 66.9 | 59.2 | 49.2 |
| 1024 | 37.0 | 108.0 | 112.0 | 97.7 | 82.3 |

Thus, all monamines are stronger than ammonia.

We will examine some of the di- and triamines.

| | $NH(CH_3)_2$ | $NH(C_2H_5)_2$ | $N(CH_3)_3$ | $N(C_2H_5)_3$ |
|---|---|---|---|---|
| $v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ | $\mu_v$ |
| 2 | 6.88 | — | 2.63 | 4.76 |
| 128 | 55.9 | 65.8 | 23.7 | 49.7 |
| 1024 | 120.7 | 130.3 | 56.8 | 11.6 |

Dimethylamine is only a little stronger than methylamine, and, similarly, diethylamine is but little stronger than ethylamine.

The triamines are not as strong as the diamines. The results for one of the tetramines are given:—

| | $(C_2H_5)_4NOH$ |
|---|---|
| $v$ | $\mu_v$ |
| 16 | 176.2 |
| 128 | 186.4 |
| 1024 | 182.6 |

and these show that the compound is a fairly strong base; indeed, much stronger than either of the other amines.

The effect of introducing two amido groups into a compound can be seen from ethylene diamine.

| | $C_2H_4(NH_2)_2$ |
|---|---|
| $v$ | $\mu_v$ |
| 32 | 8.90 |
| 256 | 23.16 |
| 1024 | 40.91 |

It is surprising that the ethylene diamine is much weaker than the ethylamine, since two amido groups should increase the basic property. This suggests the acids of phosphorus, where the weaker acid is the one containing the greater number of oxygen atoms.

A large number of relations between composition and constitution and chemical activity have been worked out, but those already given suffice to show the nature of the relations which have been discovered. No generalization of very wide significance has been reached, and exceptions are usually present to any general statement which may be made. This work resembles, in many respects, the earlier physical chemical investigations, which had to do with problems of this same general type.

Although many exceptions appear in work of this kind, nevertheless, its value is great, since it is only step by step that we arrive at the truth, and a great many steps are required to arrive at truth in its broader relations. We will leave here the chemical side of modern physical chemistry, and turn to the application of the theory of electrolytic dissociation to a physical problem.

## APPLICATION OF THE THEORY OF ELECTROLYTIC DISSOCIATION TO A PHYSICAL PROBLEM

The theory of electrolytic dissociation has not been applied as widely to physics as it has been to chemistry. This, from the nature of the case, was to be expected. Ions are the main, if not the sole factors in chemical activity; while molecules are generally the units with which the physicist has to deal.

That chapter of physics, which is most concerned with ions, is the one which has to do with electrical phenomena, and, especially, with electricity as generated in primary cells. Here, one of the essential agents is a solution of some electrolyte, or solutions of more than one electrolyte, and these solutions are always more or less dissociated. The ions are, thus, essential to the action of such cells, and here our theory bears directly upon a problem which is, indeed, a physical one.

## THE SEAT OF THE ELECTROMOTIVE FORCE IN PRIMARY CELLS

The question as to the origin of the electromotive force in primary cells is as old as the cell itself. Volta concluded that the main source of the electromotive force was at the point of contact of the two metals. Others have supposed that the contact of the two solutions was the chief source of the electromotive force. Others, again, sought for the electromotive force of such elements, at the points of contact of the electrodes with the electrolytes. The question was unsettled when the theory of electrolytic dissociation was proposed. We shall see that this

theory has furnished us with a solution to this problem, and we now have a pretty clear conception of what takes place in the primary cell.

The application of the van't Hoff laws of osmotic pressure, and the Arrhenius theory of electrolytic dissociation, to explain the action of the cell, we owe to Nernst,[1] who did this epoch-making work while in the laboratory of Ostwald in Leipzig.

It will be assumed that the reader is familiar with the method of measuring the electromotive force of elements. The method, in general, is to balance the cell in question against one of standard electromotive force, such as the Clarke element, by means of a convenient resistance box, and using the Lippmann electrometer to determine the point of equilibrium. We will not spend more time upon this experimental side of the problem, but proceed at once to the calculation of the electromotive force of elements.

**Calculation of Electromotive Force from Osmotic Pressure.** — The method of calculating electromotive force from osmotic pressure is given essentially as deduced by Ostwald[2] from the work of Nernst.

If we allow a substance to pass, isothermally, from one condition to another, the maximum amount of external work is always the same, regardless of how this takes place, whether osmotically, or electrically, or in any other way. If we know the maximum external work which is obtainable from a process, we know the amount of electrical energy; and, as we shall see, the electromotive force is calculated directly from the electrical

[1] Ztschr. phys. Chem., 4, 129. [2] Lehr. d. allg. Chem., II, p. 825.

energy. The first step is, then, to determine the maximum external work which is obtainable in a given process. This can be done by allowing the substance to pass, at constant temperature, in a reversible manner, from one condition over to the other.

Given a gas under a pressure $p_1$, and volume $v$, and allow it to expand isothermally to a pressure $p_2$. When a gas expands isothermally it takes up heat, and gives it up as volume energy. The energy set free under these conditions is: —

$$-\int_{p_1}^{p_2} v\,dp.$$

But $pv = RT$, where $R$ is the gas constant and $T$ the absolute temperature, whence the above expression becomes for gram-molecular weights: —

$$-RT\int_{p_1}^{p_2}\frac{dp}{p},$$

which expresses the volume energy obtained under the condition.

This becomes on integration: —

$$-RT\ln{}^{*}\frac{p_1}{p_2}.$$

This amount of energy, which is converted into work by an ideal gas in passing from pressure $p_1$ to pressure $p_2$, is exactly equal to the work obtained from an ideal solution

* ln is natural logarithm.

under the same conditions. That is, a solution of volume $v$ passing, isothermally, from an osmotic pressure $p_1$ to an osmotic pressure $p_2$.

But with the movements of the ions, we have the movements of the electrical charges which they carry. And, from what has been said, the amounts of work corresponding to the movements of the ions can be transformed into electrical energy.

We have, then, shown, thus far, how to calculate the maximum external work obtainable, when a solution of osmotic pressure $p_1$ passes isothermally and reversibly over to osmotic pressure $p_2$, and the relation between this work and the electrical energy obtainable.

But knowing the electrical energy, how can we determine the electromotive force? Electrical energy, like every other manifestation of energy, can be factored into an intensity and a capacity factor. The intensity factor of electrical energy is the electromotive force, or potential, and the capacity factor the amount of electricity. If we call the former $\pi$, and the latter $e_0$, we have the energy electric $e_e = \pi e_0$. If we know $e_e$, we can calculate $\pi$ at once, since $e_0$ is known from Faraday's law. Knowing the quantity of ions which pass from one osmotic pressure over to the other, we know the amount of electricity $e_0$; knowing $e_e$, we calculate $\pi$.

Let us deal with a gram-molecular weight of univalent ions. These will carry 96,540 coulombs of electricity, and this quantity we will now designate by $e_0$. If the ions are bivalent they will carry twice as much; if trivalent three times, and so on. Let us represent the valence of the ions by $v$; then a gram-molecular weight will carry $ve_0$

amount of electricity. Suppose a gram-molecular weight of these ions is charged $\pi$ potential. The amount of electrical energy required to effect this charge is: —

$$\pi v e_0.$$

But this electrical energy is equal to the osmotic, calculated above, where a gram-molecular weight was taken into account. We have: —

$$\pi v e_0 = - RT \ln \frac{p_1}{p_2}, \text{ or}$$

$$\pi = - \frac{RT \ln \frac{p^1}{p^2}}{v e_0}.$$

This is the fundamental equation for calculating the electromotive force of elements, from the osmotic pressures of the electrolytes around the electrodes.

This equation has been very much simplified by Ostwald,[1] by introducing numerical values wherever it is possible.

$R = 2$ calories, and 1 calorie $= 4.18 \times 10^7$ ergs. $T$, the absolute temperature, can be taken as 290°C. for the average conditions. The constant $\frac{RT}{e_0} = 0.0251$ volt, since volt $\times$ coul $= 10^7$ ergs.

The above equation then becomes: —

$$\pi = \frac{0.0251}{v} \ln \frac{p_1}{p_2},$$

or in case the ions are univalent: —

$$\pi = 0.0251 \ln \frac{p_1}{p_2}.$$

[1] Lehrb. d. allg. Chem., II, p. 827.

Thus far we have been using the natural logarithm obtained in the process of integration, which we have written ln. It is far more convenient in practice to use the Briggsian. To pass from the former to the latter we must divide the above constant by 0.4343, when we obtain 0.058.

The final expression of the general formula for calculating the electromotive force of an element, from the osmotic pressure of the electrolytes around the electrodes, is then: —

$$\pi = 0.058 \log \frac{p_1}{p_2},$$

where log is the Briggsian logarithm. If the valence of the ion is greater than one, this must be divided by the valence. Before attempting to apply this expression to any concrete cases, we must examine another conception introduced by Nernst.

**Electrolytic Solution-tension.** — We are perfectly familiar with the fact that when a solid or liquid is evaporated, the molecules pass into the space above the liquid; and equilibrium is established, for a given temperature, when the vapor exerts a certain definite pressure. This pressure is designated as the vapor-tension, or vapor-pressure, of the substance in question.

Says Nernst:[1] "If, in accordance with van't Hoff's theory, we assume that the molecules of a substance in solution exist also under a definite pressure, we must ascribe to a dissolving substance in contact with a solvent, similarly, a power of expansion, for here, also, the molecules are driven into a space, in which they exist under a certain

[1] Ztschr. phys. Chem., 4, 150.

pressure. It is evident that every substance will pass into solution until the osmotic partial pressure of the molecules in the solution is equal to the 'solution-tension' of the substance."

Nernst thus introduced the conception of solution-tension; and, at the same time, called attention to the close analogy between evaporation and solution, which can be seen only through a knowledge of the osmotic pressure of solutions. The metals, like many other substances, have the possibility of passing into solution as ions. Every metal, in water, has, then, a certain solution-tension peculiar to itself, and we will designate this by $P$.

If we dip a metal into pure water, let us see what will take place. In consequence of the solution-tension of the metal, some ions will pass into solution. When metallic atoms pass over into ions, they must secure positive electricity from something. They take it from the metal itself, which thus becomes negative. The solution becomes positive, because of the positive ions which it has received. At the plane of contact of the metal and solution, there is formed the so-called electrical double layer, whose existence was much earlier recognized by Helmholtz.[1] The positively charged ions in the solution and the negatively charged metal attract one another, and a difference in potential arises. The solution-tension of the metal tends to force more ions into solution, while the electrostatic attraction of the double layer is in opposition to this. Equilibrium is established when these two forces are equal. Since the ions carry such enormous charges, the number which will pass into solution before equilibrium is

[1] Wied. Ann., 7, 337 (1879).

established is so small that they cannot be detected by any ordinary method. When we are dealing with a metal immersed in pure water, it is evident that the difference in potential which obtains in the double layer is conditioned only by the magnitude of the solution-tension of the metal in question.

If we dip a metal of solution-tension $P$, into a solution of one of its salts, the case is not quite as simple. Let the osmotic pressure of the metallic ions in the solution of the salt be $p$, then either of three conditions may exist. The solution-tension may be greater than the osmotic pressure, less than the osmotic pressure, or just equal to it. We may have: —

$$P > p. \tag{1}$$

$$P < p. \tag{2}$$

$$P = p. \tag{3}$$

Let us first take case No. 1, where a metal of solution-tension $P$ is immersed in a solution of one of its salts, in which the osmotic pressure $p$ of the metallic ions is less than its own solution-tension.

At the moment the metal touches the solution, a number of metallic ions, which always carry a positive charge, will pass into solution. These ions have carried positive electricity from the metal into the solution, and the metal has thus become negative, the solution positive. At the places where the metal and solution come in contact, the double layer is formed, due to the attraction of the opposite charges.

"This double layer has a component of force, which acts at right angles to the plane of contact of the metal

and solution, and tends to drive back the metallic ions from the electrolytes to the metal. It acts in direct opposition to the electrolytic solution-tension."[1]

The condition of equilibrium is reached when these two opposing forces just equalize one another; and the final result is the existence of an electromotive force between the metal and the solution, the metal being negative, the solution positive.

It is clear that a metal cannot throw as many ions into a solution of its salt, as into pure water, because the osmotic pressure of the metallic ions already in the solution acts against the solution-tension of the metal.

Let us now take the second case; where the solution-tension of the metal is less than the osmotic pressure of the metallic ions in the solution. Metallic ions will separate from the solution upon the metal. When a metallic ion passes over into an atom it gives up its positive charge, and in this case it gives it up to the metal, which becomes positive. The solution, having lost some of its positively charged ions, becomes negative. At the points of contact of solution and metal, we have again the electrical double layer, but this time the metal is positive and the solution negative, which is exactly the reverse of the case first considered. Metal ions will separate from the solution until the electrostatic component of force of the double layer, at right angles to the plane of contact of metal and solution, is just equal to the excess of the osmotic pressure over the solution-tension. Equilibrium is established when the sum of the solution-tension of the metal and this component of force is just equal to the osmotic pressure of the metallic

[1] Ztschr. phys. Chem., 4, 151.

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ions in the solution. An electromotive force exists here, also, between the metal and the solution, but in the reverse direction from the case first considered.

The third case is where the solution-tension of the metal is just equal to the osmotic pressure of the metallic ions in the solution. Just as soon as the metal touches the solution, equilibrium is established. Ions neither dissolve from the metal, nor separate from the solution. There is no double electrical layer formed, and there is no difference in potential between the metal and the solution.

If now we inquire which metals have high, and which low solution-tensions, we will find that magnesium, zinc, aluminium, cadmium, iron, cobalt, nickel, and the like, are always negative when immersed in solutions of their own salts. This means that the solution-tension of the metal is always greater than the osmotic pressure of the metal ion, in any solution of their salts which can be prepared. If, on the other hand, we take gold, silver, mercury, copper, etc., we usually find the metal positive when immersed in a solution of its salt. This means that the solution-tension of the metal is so small, that it is less than the osmotic pressure of the metallic ion in the solution. When a very dilute solution of salts of these metals is prepared, the osmotic pressure of the metallic ion may become less than the very slight solution-tension of these metals; and then the metal would be negative with respect to its solution.

We have, thus far, spoken chiefly of the solution-tension of metals, which tends to drive the metal over into cations. Substances which can pass over into anions have also a

solution-tension, as is pointed out by Le Blanc.[1] If the chlorine ions in a solution had an osmotic pressure which was greater than the solution-tension of chlorine, the chlorine ions would pass over into ordinary chlorine. But Le Blanc adds, that, as far as we know, all substances which can yield negative ions have a high solution-tension.

**Constancy of Solution-tension.** — It was supposed for a time, that the solution-tension of a metal is a characteristic constant for the substance. This view was held by Ostwald and developed in his Lehrbuch. On page 852 it is stated that "the value $P$, of the electrolytic solution-pressure, is a constant peculiar to the metal, which depends upon the temperature only, and generally increases with increasing temperature."

So far as we know, this holds for a given solvent, but does not apply to different solvents.[2] Jones has found that the solution-tension of metallic silver, when immersed in an alcoholic solution of silver nitrate, is only about one-twentieth of that in an aqueous solution. We can, therefore, regard solution-tension as a constant only for any given solvent in which the salts of the metal are dissolved. Indeed, this is what we would expect, when we consider that nearly every substance dissolves differently in, or has a specific solution-tension towards, every solvent. If the substances which dissolve readily in solvents, vary so greatly from solvent to solvent, as we know they do, why should not substances which are only slightly soluble, such as the metals, show this same difference?

**Calculation of the Difference in Potential between Metal**

[1] Lehrb. der Elektrochemie, p. 121.
[2] Ztschr. phys. Chem., 14, 346; Phys. Rev., 2, 81.

**and Solution.** — The difference in potential between a metal of solution-tension $P$, and a solution of one of its salts in which the metal ion has an osmotic pressure $p$, can be calculated as follows.

When a substance of solution-tension $P$ is converted into ions of osmotic pressure $P$, no work is done. Therefore, to convert a substance of solution-tension $P$ into ions of osmotic pressure $p$, the maximum work to be obtained is the same as that obtained by transferring the ions from osmotic pressure $P$ to osmotic pressure $p$. Now we have seen that the gas laws apply to the osmotic pressure of solutions, and the amount of work can be calculated from a gas in passing from gas pressure $P$ to gas pressure $p$. If we deal with a gram-molecular weight, we have seen (p. 228) this to be: —

$$RT \ln \frac{P}{p}.$$

We have seen that this osmotic work is equal to the electrical work for an isothermal transformation. The electrical work is the potential times the amount of electricity. If we are dealing with gram-molecular quantities, it is $\pi v e_0$.

Equating these two values, we have: —

$$\pi v e_0 = RT \ln \frac{P}{p},$$

or, if the ions are univalent, $v = 1$, when we have: —

$$\pi = \frac{RT}{e_0} \ln \frac{P}{p}.$$

Now we know, from page 230, that $\frac{RT}{e_0} = 0.0251$ volt. Passing from natural to Briggsian logarithms, this becomes 0.058 volt.

The potential between metal and solution is, then, when $T = 290°$ : —

$$\pi = 0.058 \log \frac{P}{p}.$$

We have learned, thus far, how to calculate the electromotive force of elements from the osmotic pressures of the solutions around the electrodes; and also how to calculate the potential between a metal and the solution of one of its salts in which the metal is immersed. With these two conceptions in mind, we will now study a few elements to see how these principles are applied.

**Types of Cells.** — If the chemical process in the cell remains the same during the time it is closed, the cell is *constant.* If the chemical process changes, it is *inconstant.*

Constant elements differ among themselves. Through some of these we can send a current in the opposite direction without changing their electromotive force. This class of constant elements is termed *reversible.* This applies to elements in which the electrodes are immersed in solutions of their salts. Take as an example the Daniell element. This consists of a bar of zinc immersed in a solution of zinc sulphate, and a bar of copper in a solution of copper sulphate. When the current is passed in the opposite direction through this cell, its nature is not changed. The normal action is that the zinc dissolves and copper separates. When a current is passed in the opposite

direction, copper dissolves and zinc separates. But neither process changes the nature of the cell.

**Concentration Elements of the First Type.** — We will first consider a very simple type of a reversible element, the two electrodes being of the same metal, and are immersed in solutions of the same salt of that metal, the solutions having different concentrations. To take a concrete example: Two bars of metallic zinc are immersed in solutions of zinc chloride, the one bar in a tenth-normal solution of the salt, the other in a hundredth-normal solution. The two solutions are connected by a tube filled with either solution. When the two zinc bars, which are the electrodes, are connected externally, the current flows, and we have an element. Ostwald defines a cell or element as any device in which chemical energy is converted into electrical.

The only difference between the two sides of this element is in the concentration of the electrolytic solutions. The element is, therefore, termed a "concentration element." Further, since the salt of the metal is *soluble*, this is termed a "concentration element of the first class," to distinguish it from other concentration elements which will be taken up later.

Take the example given above, of two bars of zinc in two solutions of zinc chloride of different concentrations. The action of the cell is such as to make the two solutions become more and more nearly of the same concentration. The more dilute solution becomes more concentrated, and the more concentrated more dilute, until when the two become equal the element ceases to act. Zinc then passes into solution in the more dilute solution, and zinc ions

separate as metal on the bar from the more concentrated solution. The electrode in the more concentrated solution is always positive, since metallic ions are giving up their positive charges to it, and separating as metal upon it. The electrode in the more dilute solution is negative, because ions are passing from it into the solution, and carrying with them positive charges, which come from the electrode. In an element of this kind, the current always flows on the outside, from the electrode which is immersed in the more concentrated solution.

The action of this cell is just what we would expect. The solution-tension of the zinc is the same on both sides of the cell. The osmotic pressure of the zinc ions is, of course, greater in the more concentrated solution. The osmotic pressure, which works directly against the solution-tension, will cause the ions to separate from the solution in which this pressure is the greater. The electromotive force of such an element would be the difference in the potential upon the two sides of the cell.

$$\pi = \frac{RT}{v} \ln \frac{P}{p_2} - \frac{RT}{v} \ln \frac{P}{p_1} = \frac{RT}{v} \ln \frac{p_1}{p_2}.$$

Here $v$ is the valence of the cation, $p_1$ and $p_2$ the osmotic pressures of the zinc ions in the two solutions. This, however, does not take into account the changes in the concentrations of the solutions, which are taking place while the current is passing.

If $e_0$ electricity passes from the electrode into the electrolyte, a gram-molecular weight of univalent cations separates from the electrode, dissolves, and increases by unity the concentration around this electrode. But, at

the same time, cations are moving from this electrode, with the current, over towards the other electrode. The amount depends upon the relative velocities of anion and cation. If we represent the relative velocity of cation by $c$, and of anion by $a$, the number of the cations which will move over with the current is $\frac{c}{c+a}$. The increase in the concentration, due to a gram-molecular weight of cations passing into solution, is then:—

$$1 - \frac{c}{c+a} = \frac{a}{c+a}.$$

This factor is to be multiplied into the former equation to obtain the osmotic work, which can then be equated to its equal, the electrical energy. Let $n_i$ represent the number of ions in the electrolyte:—

$$\pi = \frac{a}{c+a} \frac{n_i RT}{ve_0} \ln \frac{p_1}{p_2};$$

or,

$$\pi = \frac{a}{c+a} \frac{n_i}{v} 0.0002\, T \log \frac{p_1}{p_2}.$$

According to this formula, the only variables are $p_1$ and $p_2$, the osmotic pressures of the cation in the two solutions around the electrodes. The electromotive force of such elements should depend only upon the relative osmotic pressures of the solutions, and not upon the absolute osmotic pressures. This has been found to be true. The electromotive force should also be independent of the kind of zinc salt used, provided the salt is soluble, and yields the same number of zinc ions in each solution as the salt in question. Thus the chloride could be replaced by the bromide, iodide, nitrate, etc., of such

concentration that the osmotic pressure of the zinc ions remained the same, and the electromotive force of the element should remain unchanged, and such again is the fact. The reason for this will be seen at once by examining the last equation; since it is only the osmotic pressure of the cations which comes into play — the anion having nothing whatever to do with the electromotive force of the element.

The electromotive force of a number of elements of the type we are considering has been measured, and to within the limits which could reasonably be expected has been found to agree with that calculated from the above equation. To calculate the electromotive force, a number of quantities must be measured. $c$ and $a$, the relative velocities of cation and anion, must be determined; similarly, $p_1$ and $p_2$, the osmotic pressures of the cations in the solutions, must be ascertained by indirect methods, which involve the measurement of the dissociation of these solutions. Since each of these processes introduces an error of greater or less magnitude, we could not expect a very close agreement between the electromotive force as measured and as calculated. When we take all of these facts into account the agreement is often surprisingly close.

The following results, obtained by Moser, for solutions of copper sulphate, with copper electrodes, are cited by Ostwald.[1] The concentrations of solutions, I and II, are the number of parts of water to one part of copper sulphate. $\pi$ is the electromotive force expressed in thousandths of a Daniell cell. The unit is 0.0011 volt.

[1] Lehrb. d. allg. Chem., II, p. 833.

| I | II | $\pi$ Observed | $\pi$ Calculated |
|---|---|---|---|
| 128.5 | 4.208 | 27 | 27.4 |
| | 6.352 | 25 | 23.8 |
| | 8.496 | 21 | 21.4 |
| | 17.07 | 16 | 15.8 |
| | 34.22 | 10 | 10.3 |

The concentration of one solution was maintained constant throughout, and that of the other varied at will. The agreement in these cases is very satisfactory.

**Concentration Elements of the Second Type.** — The characteristic of the element which we have just been considering is that the metal is surrounded by one of its soluble salts. We may also have concentration elements in which the metal is surrounded by one of its *insoluble* salts; thus, silver surrounded by silver chloride. In the latter case we must have present, in addition, a soluble chloride; and the soluble chloride must be of different concentrations on the two sides of the cell. The element would consist then of a bar of silver, surrounded by solid silver chloride, and over this a solution of some chloride, say potassium chloride; and on the other side, a bar of silver surrounded by solid silver chloride, and over this a solution of potassium chloride, of different concentration from that used on the side first described.

This element is termed a concentration element of the second class.

The action of this cell will be such as to dilute the more concentrated solution of potassium chloride, and to concentrate the more dilute solution. Silver dissolves from the electrode surrounded by the more concentrated potassium chloride, and the ions of silver unite with the

chlorine ions, and solid silver chloride is formed. The potassium ions move with the current over to the other side of the element, and form potassium chloride with some of the chlorine which was there in combination with silver as silver chloride. This silver then separates as metal upon the electrode. In this way the more concentrated potassium chloride becomes more dilute, and the more dilute becomes more concentrated.

The electrode immersed in the more concentrated potassium chloride is the one from which silver ions separate; therefore, this is the negative pole. The pole in the more dilute solution of potassium chloride, receiving silver ions, is positive. The current then flows upon the outside, from the pole in the more dilute potassium chloride, to the pole in the more concentrated.

This is exactly the reverse of what takes place in a concentration element of the first type. There, as we have seen, the current flows on the outside, from the pole surrounded by the more concentrated electrolyte.

The electromotive force of a concentration element of the second type is calculated in a manner perfectly analogous to that employed with concentration elements of the first type. The electromotive force $\pi$ is equal to the difference in the potential at the two poles: —

$$\pi = \frac{RT}{v} \ln \frac{P}{p_2} - \frac{RT}{v} \ln \frac{P}{p_1} = \frac{RT}{v} \ln \frac{p_1}{p_2}.$$

As in the case of the concentration element of the first class, this does not take into account the changes in the concentrations of the electrolytes which are taking place. At the anode the metallic silver is passing into solution,

and when $e_0$ electricity is allowed to flow, a gram-molecular weight of the silver will pass over into ions — will dissolve. This will change the concentration of the potassium chloride around this pole by $-1$. But at the same time potassium is moving with the current, and chlorine in the opposite direction, and this further changes the concentration. If we represent the relative migration velocities of $\overset{+}{K}$ and $\overset{-}{Cl}$, respectively, by $c$ and $a$, the total change in concentration around the anode will be: —

$$-1+\frac{a}{c+a}=-\frac{c}{c+a}.$$

The change in concentration around the cathode would be, of course: —

$$+\frac{c}{c+a}.$$

This factor: —

$$-\frac{c}{c+a},$$

must be multiplied into the above expression for electromotive force; when we have: —

$$\pi=-\frac{c}{c+a}\,\frac{n_i RT}{ve_0}\ln\frac{p_1}{p_2};$$

$$\pi=-\frac{c}{c+a}\,\frac{n_i}{v}\,0.0002\,T\log\frac{p_1}{p_2};$$

where $n_i$ is, as before, the number of ions yielded by the electrolyte, and $v$ the valence of the cation. The electromotive force of a number of such elements has been measured by Nernst.[1] Mercury was used as the metal, since it could easily be obtained in pure condition.

[1] Ztschr. phys. Chem., 4, 159.

It was covered with an insoluble salt of mercury, and the soluble electrolyte then added. The chloride, bromide, acetate, and hydroxide of mercury were used, and the soluble electrolyte on both sides of the cell must contain the same anion as the salt of mercury which was employed. If the chloride was used, the soluble electrolyte must be a chloride. If the hydroxide of mercury was employed, a soluble hydroxide must be used, and so on.

Some of the combinations which were made and measured by Nernst are given in the following table. The first column contains the soluble electrolyte which was employed. Columns II and III give the concentrations of the solutions of this electrolyte on the two sides of the cell. "$\pi$ calculated" is the electromotive force calculated from the preceding formula, and "$\pi$ found" is the electromotive force of the combination, as measured by Nernst.

| I<br>Soluble<br>Electrolyte | II<br>Concentration 1 | III<br>Concentration 2 | $\pi$<br>Calculated | $\pi$<br>Found |
|---|---|---|---|---|
| HCl | 0.105 | 0.018 | 0.0717 | 0.0710 |
| HCl | 0.1 | 0.01 | 0.0939 | 0.0926 |
| HBr | 0.126 | 0.0132 | 0.0917 | 0.0932 |
| KCl | 0.125 | 0.0125 | 0.0542 | 0.0532 |
| NaCl | 0.125 | 0.0125 | 0.0408 | 0.0402 |
| LiCl | 0.1 | 0.01 | 0.0336 | 0.0354 |
| $NH_4Cl$ | 0.1 | 0.01 | 0.0531 | 0.0546 |
| NaBr | 0.125 | 0.0125 | 0.0404 | 0.0417 |
| $CH_3COONa$ | 0.125 | 0.0125 | 0.0604 | 0.0660 |
| NaOH | 0.235 | 0.030 | 0.0183 | 0.0178 |
| KOH | 0.1 | 0.01 | 0.0298 | 0.0348 |
| $NH_4OH$ | 0.305 | 0.032 | 0.0188 | 0.024 |

**Liquid Elements.** — It has long been known that there may be differences in potential at the contact of two solutions of electrolytes. This can be shown by constructing an element in which the two electrodes are of the same metal, and immersed in the same solution of the same electrolyte. There can, therefore, be no difference in potential between the two metals, nor between the metals and electrolytes, for the tensions between the metals and electrolytes are the same on the two sides, and act in direct opposition to one another. If two solutions of electrolytes of different concentrations are introduced into the circuit between the solutions in which the electrodes are immersed, we will have an element with a certain definite electromotive force. A typical liquid element would be the following: —

Mercury-mercurous chloride.

$\frac{n}{10}$ potassium chloride.

$\frac{n}{100}$ potassium chloride.

$\frac{n}{100}$ hydrochloric acid.

$\frac{n}{10}$ hydrochloric acid.

$\frac{n}{10}$ potassium chloride.

Mercurous chloride-mercury.

**Theory of the Liquid Element.** — The first satisfactory theory of the liquid element we owe to Nernst.[1] What is the

[1] Ztschr. phys. Chem., 4, 140.

source of the differences in potential in liquid elements? That differences in potential should exist in electrolytes there must be a lack of uniform distribution of ions. The region which is positive must contain an excess of cations, and that which is negative, an excess of anions. *The cause of this lack of uniform distribution of ions is to be found in the different velocities with which the different ions diffuse.*

Take the case of a solution of hydrochloric acid in contact with pure water. The hydrogen and chlorine ions in the solution of the acid are present in the same number. They are, therefore, under the same osmotic pressure, and are driven with the same force into the water. But they move with very different velocities, from regions of higher to those of lower osmotic pressure. Hydrogen is, as we have seen, the swiftest of all ions, and moves very much faster than chlorine. It will thus diffuse into the water more rapidly than chlorine, and will tend to separate from the chlorine. But the positive ions cannot separate from the negative ions, without producing a separation of the two kinds of electricity. There will result, therefore, electrostatic attractions between the layers, which will retard the hydrogen ions and accelerate the chlorine ions, until the two have the same velocity.

Differences in potential will result; and always in the sense, that the water or the more dilute solution will have the sign of the swifter ion. Hydrogen being the swiftest of all ions, water, or the more dilute solution of acid, is always positive with respect to the more concentrated. Next to hydrogen, in order of velocity, comes hydroxyl. Water, or the more dilute solution of a base, must, there-

fore, always be negative with respect to the more concentrated.

Nernst has shown not only how it is possible to account, qualitatively, for the differences in potential between electrolytes, but has furnished us also with a method of calculating these differences quantitatively.

Given two solutions of different concentrations of an electrolyte like hydrochloric acid, which is composed of a univalent cation and a univalent anion. Let the velocity of the cation be $c$, and that of the anion $a$. Let $p_1$ be the osmotic pressure of both ions in the more concentrated solution, and $p_2$ the osmotic pressure in the more dilute. If $e_0$ electricity is passed from the more concentrated to the more dilute solution, $\frac{c}{c+a}$ of a gram-equivalent of cations will move with the current, and $\frac{a}{c+a}$ of a gram-equivalent of anions will move against the current.

$\frac{c}{c+a}$ of cations have moved from a region of greater to one of less osmotic pressure. The work is: —

$$\frac{c}{c+a} RT \ln \frac{p_1}{p_2}.$$

But $\frac{a}{c+a}$ of anions have moved from a region of lower into one of higher osmotic pressure. The work done upon them is: —

$$\frac{a}{c+a} RT \ln \frac{p_1}{p_2}.$$

The total gain is the difference between these two: —

$$\frac{c-a}{c+a} RT \ln \frac{p_1}{p_2}.$$

Equating this against the electrical energy $\pi e_0$, we have: —

$$\pi = \frac{c-a}{c+a} \frac{RT}{e_0} \ln \frac{p_1}{p_2};$$

or,

$$\pi = \frac{c-a}{c+a} 0.0002\ T \log \frac{p_1}{p_2}.$$

If $c$ is greater than $a$, the more dilute solution is positive, as already stated, and the current flows on the outside, from the more dilute solution to the more concentrated. If $a$ is greater than $c$, the more dilute solution is negative, and the current flows in the opposite direction.

If the velocities of the two ions are equal ($c = a$), the right member of the above equation becomes zero, and there is no electromotive force. It is, therefore, impossible to construct a liquid element from solutions of an electrolyte whose cation and anion have the same velocities. If the valence of either ion is greater than unity, this must be taken into account. If we represent the valence of the cation by $v$, and that of the anion by $v_1$, the above expression becomes: —

$$\pi = \frac{\frac{c}{v} - \frac{a}{v_1}}{c+a} 0.0002\ T \log \frac{p_1}{p_2}.$$

Nernst prepared liquid elements and determined their electromotive force. He then calculated the electromotive force from the above equation, and compared the values found experimentally with those from calculation.

The following element already referred to was constructed: —

$$\mathrm{Hg-HgCl-KCl}\overset{1}{-}\mathrm{KCl}\overset{2}{-}\mathrm{HCl}\overset{3}{-}\mathrm{HCl}\overset{4}{-}\mathrm{KCl-HgCl-Hg}.$$

$$\frac{n}{10} \quad \frac{n}{100} \quad \frac{n}{100} \quad \frac{n}{10} \quad \frac{n}{10}.$$

The potential differences at the ends are equal and opposite, and therefore equalize one another. The four differences in potential which must be taken into account are indicated above. But the potential differences are dependent upon the relative not upon the absolute osmotic pressures. The potentials at 2 and 4 are, therefore, equal and opposite, and can also be left out of account. This leaves the potentials at 1 and 3, and these can be calculated by the method already given. Let $c_1$ and $a_1$ be the relative velocities of potassium and chlorine ions, and $c_2$ and $a_2$ the relative velocities of hydrogen and chlorine ions; the electromotive force of this element would be calculated as follows, from the equation just deduced. The electromotive force would be the difference between these two potentials: —

$$\pi = \frac{c_1 - v_1}{c_1 + v_1} \frac{RT}{e_0} \ln \frac{p}{p_1} - \frac{c_2 - v_2}{c_2 + v_2} \frac{RT}{e_0} \ln \frac{p'}{p_1'}.$$

$p$ and $p_1$ are the osmotic pressures of the potassium and chlorine ions in the more concentrated and more dilute solutions, respectively; $p'$ and $p_1'$ the osmotic pressures of the hydrogen and chlorine ions in the solutions of hydrochloric acid.

$$\frac{p}{p_1} = \frac{p'}{p_1'}.$$

Introducing this into the last equation, we have: —

$$\pi = \left(\frac{c_1 - a_1}{c_1 + a_1} - \frac{c_2 - a_2}{c_2 + a_2}\right) \frac{RT}{e_0} \ln \frac{p}{p_1};$$

or,
$$\pi = \left(\frac{c_1 - a_1}{c_1 + a_1} - \frac{c_2 - a_2}{c_2 + a_2}\right) 0.0002\, T \log \frac{p}{p_1}.$$

This is the expression for calculating the electromotive force in liquid elements, like the above, where the valence of the cation is the same as that of the anion. If they are different, we will represent the valence of the cations by $v$ and $v'$, and that of the anions by $v_1$ and $v_1'$; the equation for the electromotive force would then become: —

$$\pi = \left( \frac{\frac{c_1}{v} - \frac{a_1}{v_1}}{c_1 + a_1} - \frac{\frac{c_2}{v'} - \frac{a_2}{v_1'}}{c_2 + a_2} \right) 0.0002\ T \log \frac{p}{p_1}.$$

The electromotive force of the liquid elements which have been studied, as calculated from the above equation, agrees with that measured, to within the limits of experimental error.

It should be observed, that the expression deduced above holds only for the potential at the contact of solutions of the same electrolyte, the solutions being of different concentrations. If different electrolytes are used, we have no general means of calculating the potential at their surface of contact.

It should be stated before leaving the subject of liquid elements, that the potential at the contact of two solutions is usually not great, and that the electromotive force of liquid elements is in general not large.

**Sources of Potential in a Concentration Element.** — We may now analyze, more closely, the electromotive force in a concentration element, in the light of what we have learned about the liquid element. Thus far, we have dealt with the concentration element as if the only sources of the potential were at the points of contact of the electrodes and the solutions. And indeed this is practically true in

the cases of the concentration element which we have studied.

We have learned from the study of the liquid element, that the plane of contact of two solutions of an electrolyte is also a seat of potential. In the concentration element there is always such a contact between two solutions of the electrolyte, and this must be a source of potential. In the concentration element which we have studied, this potential is so small that it can practically be neglected. While the potential between solutions is usually small, it may, however, easily assume proportions which must be taken into account. We must now see how it is possible to calculate the potential at the contact of the two solutions in the concentration element. We can then analyze the electromotive force of a concentration element into its three constituents, and calculate the magnitude of the potential at each electrode, and also at the surface of contact of the electrolytes.

Let the potential at one electrode be $\pi'$, at the other electrode $\pi''$, and at the contact of the two electrolytes $\pi'''$. The values of these potentials are calculated by means of the following formulas: —

$$\pi' = 0.0002\ T \log \frac{P}{p_1};$$

$$\pi'' = -\ 0.0002\ T \log \frac{P}{p_2};$$

$$\pi''' = 0.0002\ T \frac{c-a}{c+a} \log \frac{p_1}{p_2}.$$

These equations obtain for univalent ions. If the valence of the ion is greater than one, this must be taken

into account in the way already described. The sum of the three potentials must then be the potential of the concentration element.

$$\pi' + \pi'' = -\,0.0002\ T \log \frac{p_1}{p_2};$$

$$(\pi' + \pi'') + \pi''' = 0.0002\ T\ \frac{2\,a}{c + a} \log \frac{p_2}{p_1}$$

This must be the same as the equation already deduced (p. 241) for the concentration element. It will be seen to be the case, if we consider that $n_i = 2$, and $v$ for univalent ions equals 1.

We can thus calculate the magnitude of the three sources of potential in a concentration element of the first class. An element of this class has been chosen, since the relations are somewhat simpler. The main sources of potential are at the contact of electrode and electrolyte, while a very small potential exists at the contact of the two electrolytes. In elements of this kind, it is perfectly clear that there is no potential where the two electrodes come in contact, because these are of the same metal.

**The Electromotive Force of the Daniell Element.** — The elements which we have considered thus far have both electrodes of the same metal. The solution-tension of the metal was, therefore, the same upon both sides of the cell, and being of equal value and opposite sign, it disappeared from the equation for the electromotive force of the element.

In most of our common elements, however, two metals are used as electrodes, or a metal and carbon. It is evident that in these cases the solution-tension of the electrode

must be taken into account, since it is different for different metals.

The Daniell element is taken as a type of the two metal elements with which we are so familiar. The application of our fundamental equation to this element will serve as an example of the way in which it may be applied to other well-known elements.

The Daniell element consists of zinc in zinc sulphate, and copper in copper sulphate. Zinc dissolves and copper separates from the solution. The zinc electrode is therefore negative, and the copper positive, the current passing on the outside from the copper to the zinc. The electromotive force is equal to the difference in potential at the two electrodes, since the potential at the contact of the zinc sulphate and copper sulphate is so slight that we can practically disregard it.

Representing the potential at the two electrodes by $\pi_1$ and $\pi_2$, we have: —

$$\pi_1 = \frac{RT}{2e_0} \ln \frac{P}{p};$$

$$\pi_2 = \frac{RT}{2e_0} \ln \frac{P_1}{p_1};$$

in which $P$ and $P_1$ are the solution-tensions of the two metals.

$$\pi_1 - \pi_2 = \pi = \frac{RT}{2e_0}\left(\ln \frac{P}{p} - \ln \frac{P_1}{p_1}\right).$$

In the light of this example, the application of the conceptions here developed, to other special cases, should be a simple matter.

**The Gas-battery.** — The typical gas-battery consists of an electrolyte, two gases which can act chemically upon one another, and two platinum electrodes which are partly surrounded by the electrolyte, and partly by the gases.

Take as a simple example, hydrogen over one electrode and chlorine over the other, the electrolyte hydrochloric acid, and the electrodes platinum. Hydrogen and chlorine will pass into solution at the two poles until there is an equilibrium between the force driving these substances into solution (solution-tension), and the osmotic pressure of the hydrochloric acid solution, which acts against the above-named force. The hydrogen pole is negative, since the solution-tension of the hydrogen is greater than the osmotic pressure of the solution; the hydrogen atoms becoming ions by taking positive electricity from the platinum electrode, which thus becomes negative. Exactly the opposite result is obtained at the other electrode, chlorine atoms becoming ions by taking negative electricity from the electrode, which therefore becomes positive.

Ostwald[1] has shown that the theory of Nernst can be applied also to the electromotive force of the gas-battery. He has worked out even a simpler case than the one given above. We will take up first the simplest possible case, where we have the same gas, say hydrogen, over both electrodes, the hydrogen upon the two sides being at different pressures.

The action of such an arrangement would be, as Ostwald shows, to equalize the pressure of the gas upon the two sides of the cell. Hydrogen must pass into solution as ions upon the side where it is under the greater

[1] Lehrb. d. allg. Chem., II, p. 895.

pressure, and ions of hydrogen must separate as gas upon the other side of the cell. Upon the side where hydrogen atoms are becoming ions, they take positive electricity from the electrode, which becomes negative, and the other electrode positive, because positive hydrogen ions are giving their charges up to it. We have here an analogue of the concentration element, and the electromotive force can be calculated in a similar manner.

The electromotive force of this element also is the difference in the potential upon the two sides: —

$$\pi = \frac{RT}{ve_0} \ln \frac{P}{p_2} - \frac{RT}{ve_0} \ln \frac{P}{p_1};$$

where $P$ is the solution-tension of hydrogen, and $p_1$ and $p_2$ the pressures of the hydrogen gas upon the two sides. The solution-tension, being the same upon both sides of the cell, disappears, as in the concentration element, and then we have: —

$$\pi = \frac{0.0002\, T}{v} \log \frac{p_1}{p_2}.$$

Since for hydrogen, $v = 2$, we have: —

$$\pi = 0.0290 \log \frac{p_1}{p_2}.$$

Ostwald [1] has also calculated the electromotive force for a gas-battery consisting of two gases. But as this has been worked out much more fully by Smale,[2] we will turn to his work.

Take the case of oxygen at one pole and hydrogen at the other.

[1] *Loc. cit.*

[2] Ztschr. phys. Chem., 14, 577, and 16, 562.

Let $P_1$ be the solution-tension of hydrogen.
Let $P_2$ be the solution-tension of oxygen.
Let $T$ be the absolute temperature.
The potential at the hydrogen pole is: —

$$\pi_1 = 0.0002\ T \log \frac{P_1}{p_1}.$$

Since the solution-tension of oxygen is negative: —

$$\pi_2 = 0.0002\ T \log \frac{p_2}{P_2};$$

$$\pi_1 - \pi_2 = \pi = 0.0002\ T \log \left(\frac{P_1}{p_1} - \frac{p_2}{P_2}\right);$$

$$\pi = 0.0002\ T \log \left(\frac{P_1}{p_1} + \frac{P_2}{p_2}\right).$$

The theoretical consequences of this equation are very interesting. $P_1$ and $P_2$, the solution-tensions of the gases, are independent of the nature and concentration of the electrolyte used on the two sides of the element; and $p_1$ and $p_2$ are practically constant for solutions of nearly the same dissociation.

Smale[1] has tested this point, using seven acids, three bases, and seven salts. The concentrations for the same electrolyte vary in most cases from 0.1 to 0.001 normal. He found that the electromotive force of the hydrogen-oxygen battery was practically constant, independent of both the nature and concentration of the electrolytes used beneath the gases.

A few results taken from the work of Smale will bring out this fact.

[1] *Loc. cit.*

| Electrolyte Used | Concentration Normal | E.M.F. |
|---|---|---|
| HCl | 0.1 | 0.998 |
| HCl | 0.01 | 1.036 |
| HCl | 0.001 | 1.055 |
| KOH | 0.1 | 1.098 |
| KOH | 0.01 | 1.095 |
| KOH | 0.001 | 1.093 |
| $K_2SO_4$ | 0.1 | 1.074 |
| $K_2SO_4$ | 0.01 | 1.069 |
| $K_2SO_4$ | 0.001 | 1.069 |

The results thus agree satisfactorily with the deduction from theory.

If, instead of oxygen, other gases, as chlorine, are used, the electromotive force depends upon the concentration of the electrolyte, which also agrees with theory, as is shown by Smale.

But the theory admits of still further experimental test.

If the electrodes are of two different metals, say platinum and palladium, and are surrounded by the same gas which does not attack them, and are immersed in the same electrolytes, the electromotive force at each electrode is in terms of the theory formulated thus: —

$$\pi_1 = 0.0002\ T \log \frac{P_1}{p_1};$$

$$\pi_2 = 0.0002\ T \log \frac{P_2}{p_2}.$$

$P_1$ and $P_2$ are the solution-tensions of the gas in platinum and palladium, respectively; $p_1$ and $p_2$ the osmotic pressures at the electrodes; which are equal in this case,

since the same electrolyte is used on both sides. Therefore, we have:—

$$\pi_1 - \pi_2 = \pi = 0.0002\ T \log \frac{P_1}{P_2} \text{ volts.}$$

The metal electrodes then play only this rôle, they offer a large surface to the gas, which facilitates its solution in them. The *electromotive force* of such an element should, therefore, be *independent of the nature of the electrode used*, since solution-tension is a constant for any given metal, according to the theory. It should, further, *be independent of the size of the electrode.*

Both of these points were tested experimentally by Smale. The nature of the electrode, whether platinum, palladium, or gold, had no influence on the electromotive force. The size of the electrode, beyond a certain point, had no influence. A certain amount of surface is, however, necessary in order that the electrode should reach its full tension.

This work of Smale furnishes then another beautiful experimental confirmation of the consequences of that theory, which has enabled us to calculate the electromotive force of concentration elements, liquid elements, etc.

A number of other types of elements might be taken up, and their electromotive force calculated from the method of Nernst, which, as we have already seen, is based upon van't Hoff's laws of osmotic pressure, and Arrhenius's theory of electrolytic dissociation. This is, however, not necessary, since the application to special cases is simple, if the fundamental principles are once grasped.

**Chemical Action at a Distance.** — Before concluding this section, we will describe a phenomenon of unusual interest. On account of its close relation to solution-tension, it should appear in this connection.

In 1891, a paper was published by Ostwald,[1] under the surprising title "Chemische Fernewirkung." It was surprising, because chemical action, as ordinarily understood, takes place only between substances which are close to one another. Ostwald begins his paper by calling attention to the fact that amalgamated zinc is not dissolved by dilute acids, but if the zinc is surrounded by a platinum wire, it is dissolved by the acid. It is not even necessary for the platinum wire to surround the zinc, for if the wire touches the zinc at any one point, solution will take place.

Ostwald suggests that the zinc and platinum wire be joined at one place, and then the free ends of both immersed in a vessel containing, say, potassium sulphate. Let a screen of some porous material be placed between these free ends of the platinum and zinc, so that the salt solution around the one is separated from that around the other. He then asks the question: To which metal must sulphuric acid be added, in order that the zinc may be dissolved by the acid?

"The question seems at first sight to be absurd; since, in order that the zinc should dissolve, it appears to be self-evident that the acid should be added to the zinc. If we carry out the experiment we find exactly the reverse to be true. The zinc does not dissolve rapidly, if acid is added to the solution of potassium sulphate around the zinc. If, on the contrary, the acid is added to the solution around

[1] Ztschr. phys. Chem., 9, 540.

the platinum, the zinc dissolves with a copious evolution of hydrogen gas. The hydrogen appears on the platinum, as is always the case when zinc is in combination with platinum. To dissolve the zinc under the conditions described, the solvents must not be allowed to act on the metal to be dissolved, but on the platinum which is in contact with the zinc."

A number of other cases are cited.

Zinc in sodium chloride behaves in the same manner, when hydrochloric acid is added to the platinum. Cadmium also behaves like zinc. Tin, surrounded by sodium chloride, dissolves when hydrochloric acid is added to the platinum. Aluminium behaves like tin. Silver connected with platinum dissolves in sulphuric acid when a few drops of chromic acid are added to the platinum. Gold dissolves in sodium chloride, if chlorine is brought in contact with the platinum.

**Experiment to demonstrate Chemical Action at a Distance.** Fill a beaker with a solution of potassium sulphate. Take a piece of glass tubing about 10 cm. long and 2 cm. wide, and close the lower end with vegetable parchment. Fit a bar of pure zinc, about 10 cm. long, tightly into a cork which just closes the top of this glass tube. Fill the glass tube with some of the same solution of potassium sulphate, and insert the bar of zinc — the cork closing the top of the glass tube. Around the top of the zinc bar above the cork wrap a piece of platinum wire of sufficient length to reach nearly to the bottom of the beaker, when the glass tube is introduced into the beaker in the manner to be hereafter described. The free end of the platinum wire should be coiled upon itself a num-

ber of times, or it is better if it is connected with a piece of platinum foil a few centimetres square, so as to expose a larger surface.

The glass tube is now immersed in the beaker until the surface of the solution in the tube is only a centimetre or two above the surface of the solution in the beaker, the free end of the platinum wire, or the platinum foil, being allowed to rest on the bottom of the beaker.

If a few drops of sulphuric acid are introduced into the potassium sulphate just around the bar of zinc, the zinc will be very slightly affected. But if a few drops of sulphuric acid are poured upon the coiled end of the platinum wire, or upon the platinum foil, the zinc will dissolve rapidly in the neutral potassium sulphate which surrounds it, and a copious evolution of hydrogen will take place from the platinum, where it is in contact with the sulphuric acid. After a few moments the presence of zinc can be demonstrated in the inner tube, by any of the well-known reactions for zinc.

As Ostwald states, similar phenomena have long been known. Nearly forty years ago Thomsen [1] described a galvanic element, which consists of copper in dilute sulphuric acid, and carbon in a chromate mixture. When the carbon and copper were connected, the metal dissolved as the sulphate, in sulphuric acid, in which copper alone is not soluble. While similar facts were known, there was no rational explanation offered to account for them, until Arrhenius proposed the *Theory of Free Ions*.

It is almost self-evident that the phenomenon is closely connected with electrical changes. Ostwald demonstrated

[1] Pogg. Ann., III, 192 (1860).

this, by introducing between the metal and the platinum a fairly sensitive galvanoscope. When the acid was added to the platinum, the presence of a current was shown by the throw of the instrument.

The explanation of this phenomenon is perfectly simple, now that we have the theory of electrolytic dissociation, and are familiar with its application to the primary cell.

When metallic zinc is immersed in a solution of a neutral salt, like potassium sulphate, it sends, in consequence of its own solution-tension, a certain number of zinc ions into the solution. The zinc is thus made negative, and the solution, which has received the positive ions, positive. This continues until a definite difference in potential between metal and solution is established. The amount of metal required to effect this condition is, as we have seen, so small that it cannot be detected by any chemical means.

The zinc cannot dissolve further, because of the excess of positive ions in the solution. In order that more zinc may pass into solution, some of these positive ions must be removed. If the zinc is in combination with another metal, such as platinum, the latter takes the same negative charge as the zinc. When the platinum is immersed in the solution, it attracts the excess of positive ions in the solution, and these collect upon the platinum.

We would expect the excess of positive ions in the solution to give up their charge to the negative platinum, and separate from the solution, or, in case of potassium, decompose the water which is present. This depends both upon the nature of the ion and of the electrode. If the positive ion is the potassium of potassium sulphate, the difference in potential produced by introducing the

zinc is not sufficient to cause this ion to lose its charge to the platinum. If sulphuric acid is added to the platinum, the difference in potential, produced by introducing the bar of zinc, is sufficient to compel the hydrogen to give up its positive charge to the platinum, and separate as ordinary hydrogen. The platinum, having received positive electricity from the hydrogen ions, conducts this over to the zinc. The zinc becomes less negative than before the hydrogen separated at the platinum, and the difference in potential between the zinc and the surrounding solution is less than before. More zinc dissolves or passes over into ions, more hydrogen ions give up their charge to the platinum and separate as gas; and this continues until all of the zinc has dissolved, or all of the hydrogen ions have separated as gas.

As Ostwald observes, this explanation shows not only why the acid must be added to the platinum and not to the zinc, but throws light also on the problem of the solution of metals in general. A word or two on this subject. It has long been known that pure zinc does not dissolve in acids, while impure zinc readily dissolves. It is quite evident that the zinc in the two cases has the same tendency to dissolve. Pure zinc dissolves readily when in contact with a metal, such as platinum, which has a small solution-tension. As we have seen from the foregoing explanation, the difference is not in the solution of the zinc, but in the ease with which the hydrogen can escape from the solution. The presence of a metal with small solution-tension allows this to take place more readily, and this is the reason that impure zinc dissolves in acids.

The reason why pure zinc does not dissolve in acids is because this metal has a strong positive solution-tension; it sends positively charged ions into solution under a high solution-tension, and, therefore, opposes the separation of any other positive ion, like hydrogen, upon it. Pure zinc, therefore, does not dissolve in acids, because the hydrogen ions cannot give up their positive charges and escape.

When a metal like platinum, which has a small solution-tension, is present, the hydrogen can easily give up its charge to this metal and escape as gas. The zinc, because of its high solution-tension, and because the hydrogen cations can so easily escape, then dissolves.

To repeat the essential steps in the explanation of the experiment described above: Pure zinc immersed in potassium (or any soluble) sulphate, to which sulphuric acid is added, or in a solution of pure sulphuric acid itself, does not dissolve, because the zinc has such a high solution-tension that the hydrogen ions cannot give up their charge to it and escape. The zinc, however, throws a few ions into solution, and becomes negatively charged. If now the zinc is connected with platinum, which has a small solution-tension, and the acid added to the platinum, the hydrogen ions can easily give up their charge to the platinum and escape as gas. The platinum, which was at the potential of the zinc with which it is in combination, now becomes positive with respect to the zinc, and a positive charge, therefore, flows from the platinum to the zinc. The zinc, having received positive electricity, can begin dissolving anew, and continue to pass into solution as long as it receives positive electricity from

the platinum — as long, therefore, as there are any hydrogen ions in the solution to furnish positive electricity to the platinum. Or, as we are accustomed to express it, as long as there is any acid in contact with the platinum.

This subject will be concluded with a paragraph from this fascinating paper by Ostwald: "We see that the usual explanation, that solution takes place *because* of galvanic currents between the zinc and the other metals, is not in strict accord with the facts. The galvanic currents are inseparably connected with the process of solution, but they are not the primary causes of the solution. They are set up, rather, by the process of solution, which they must necessarily accompany, since solution is a question of ion formation and disappearance. If it is possible for the positive ions present to separate in any way from the solvent, solution takes place."

Ostwald then goes on to show that it is not necessary for the ion to separate from the solution. The positive ion may be destroyed in the solution, or a negative ion produced; and in either case the metal will dissolve. But for these and similar facts the original paper must be consulted.

**Conclusion.** — In concluding this chapter on the calculation of the electromotive force of elements, attention should again be called to the fact, that the method worked out by Nernst was based directly upon van't Hoff's laws of osmotic pressure, and the theory of electrolytic dissociation. Without either of these conceptions the work of Nernst would have been absolutely impossible. With them, he has thrown entirely new light on the whole ques-

tion of the electromotive force of elements, and has furnished us, for the first time, with a satisfactory theory of the action of the primary cell.

## APPLICATION OF THE THEORY OF ELECTROLYTIC DISSOCIATION TO BIOLOGICAL PROBLEMS

The application of a theory of solution to biological problems is not so evident as to chemical, where solutions are always involved. Solutions are, however, very frequently used by the physiologist, and any theory of solution must, therefore, bear upon many physiological problems.

It is only in the last few years that the theory of electrolytic dissociation has found its way into physiology, and work along this line may be said to have just been begun. A few examples of the application of the theory in this direction will be given.

**Toxic Action and Electrolytic Dissociation.** — Kahlenberg and True[1] published a paper in 1896 on "The Toxic Action of Dissolved Salts and their Electrolytic Dissociation," which was the pioneer work along this line.

It had been thought that the physiological action of any substance was due to its chemical nature. In the case of a solution, all of the chemical and physical properties are a function of the properties of the ions, plus those of the undissociated molecules which it contains. It would, therefore, seem probable, that the physiological action of such solutions was due to the same cause. Many investigations on the physiological action of aqueous solutions on bacteria and higher forms of plant life, as well as on animals, have

[1] Botan. Gazette, 22, 81.

been made. In work of this kind, percentage concentration has been dealt with, and this obscures any general relations which might exist.

If a dilute solution of sodium chloride differs from a dilute solution of hydrochloric acid, in that the former contains sodium ions and the latter hydrogen ions, then the poisonous character of the latter must be due to the hydrogen ions.

Since a very dilute solution is completely dissociated, the poisonous properties of such a solution must be due to one or both of the ions which it contains, since there are no molecules present. If the toxic action of acids on plants is due only to the hydrogen ion, then solutions of different acids containing the same number of hydrogen ions should be equally poisonous. Solutions of hydrochloric acid, nitric acid, and sulphuric acid are completely dissociated at a volume of about one thousand litres; hence, solutions of these acids which are of this strength, or more dilute, should have the same toxic action; since the ions $\overline{Cl}$, $\overline{NO_3}$, $\overline{\overline{SO_4}}$, have none.

This has been tested, experimentally, for the higher plants, by finding the strength of the solution of the acid in which the root of the plant will just live. Seedlings of *Lupinus albus* L. were employed. They have a straight, clean radicle, and are well adapted to this work. The root was suspended in the acid solution, and its condition determined by the rate of growth. It was a simple matter to determine when the root was dead, since it lost its satiny lustre and acquired a dead-white color. Its appearance may be described as coagulated. The root was immersed in the solution for fifteen to twenty-four hours, which was

the time chosen for an experiment. The root of the plant was first placed in a more concentrated solution of the acid. If this was found to kill it, another root was placed in a more dilute solution, and so on, until a dilution was reached in which the root just lived. In the case of strong acids, the root would just live in a solution which contained a gram-molecular weight of the acid in 6400 litres of solution; expressed in ordinary terms, the solution had a volume of 6400 litres. This expresses the toxic action of the hydrogen ion, and it is the same for all strong acids. The hydroxyl ion was studied, and found to be far less poisonous than the hydrogen ion. The root would just live when the solution contained a gram-molecular weight of the base in 400 litres of solution. The effect of the ions of certain salts was also studied. The copper ion was especially toxic. The roots would just survive in a solution which contained a gram-molecular weight of copper ions in 51,200 litres of solution.

Whenever copper forms part of an ion, and is not the whole ion, the result is very different. Thus, in Fehling's solution copper forms part of the ion, it being in combination with an organic complex. We would expect it, therefore, to have a different action, under these conditions, than when alone. This was tested by experiment. In preparing the Fehling's solution, cane-sugar was used instead of Rochelle salt, in order to avoid the excess of other ions in the solution. An excess of caustic alkali was avoided, in order to keep out hydroxyl ions, which are known to be poisonous. The roots would grow in a solution of this salt, which contained a gram-atomic weight of copper in 400 litres. Copper, when alone as an ion, is,

thus, far more poisonous than when in combination with this complex.

Iron in its ionic state has very different toxic action than when the iron atom is combined with other things to form an ion. Thus the iron in a ferric salt has very different effect from the iron in potassium ferrocyanide. It would be indeed surprising if this were not true, since iron in a ferric salt forms a cation, while iron in potassium ferrocyanide is combined with the 6 CN groups, forming a part of the complex anion.

Cobalt and nickel have the same toxic action as iron. The question is raised, whether there is any connection between this action and the fact that the three elements have very nearly the same atomic weights. The experimental data are yet far too meagre to answer this question. Cadmium and silver also are found to be very poisonous.

The Cu ion is about as toxic as the hydrogen ion. Hydrocyanic acid is almost completely undissociated, yet it is very poisonous. The plant will stand only $\frac{1}{12800}$ of a gram-molecule per litre. This is an excellent example of how molecules as well as ions may be poisonous.

The investigation was extended to the organic acids, and these, with some exceptions, fell in line with the above relations.

This investigation has shown that the toxic action of solutions of electrolytes, which are completely dissociated, is due to the ions present. When the electrolyte is only partly dissociated, the undissociated portion may exert a toxic action. We have here a recognition of the theory of electrolytic dissociation in the organic world. The paper

of Kahlenberg and True contains the following significant passage: —

"It will be seen that a wide field for research along physiological lines opens up, by applying to the field of biology the dissociation theory which has proved so fertile in chemistry and physics. Further work in this direction, using the latest and best that the new physical chemistry has to offer, it is to be hoped, will place our knowledge of the physiological action of solutions of electrolytes on a better basis than the purely empirical one on which it has thus far rested. It does not seem too much to expect that the effect of such study will soon be felt in agriculture and therapeutics, while bacteriological study, pursued from the standpoint of the new theory, will yield important additions to our knowledge of antiseptics."

Another investigation in the same field has been carried out by F. D. Heald.[1] He studied the toxic action of acids and salts upon different plants. He used the three plants: —

*Pisum sativum*,
*Zea Mais*,
*Cucurbita Pepo*.

The conclusions of Kahlenberg were all confirmed by this work, in which more than one plant was used. Says the author, "The theory of electrolytic dissociation has thus thrown light upon the physiological action of different substances, and the theory has, itself, been strengthened by these experiments upon living things."

**Toxic Action of the Phenols and their Dissociation.** — The work begun by Kahlenberg and True has since been

[1] Botan. Gazette, 22, 125.

extended by True and Hunkle[1] to the phenols. They investigated a number of phenols, using different concentrations, and determined the greatest concentration in which the roots of *Lupinus albus* would just live and grow. The conductivity of the solutions of the different phenols was also measured. They conclude that, except in isolated instances, the electrolytic dissociation plays but a subordinate rôle in determining the toxic properties of phenylic compounds. Picric and salicylic acids are strongly dissociated, and are very poisonous because of the large number of hydrogen ions in their solutions. Electrolytic dissociation exerts a pronounced influence in the cresols and mononitrophenols.

**Dissociation and Disinfecting Action.** — In 1896 a paper appeared by Paul and Krönig,[2] describing the action of a large number of reagents on bacteria. The work was done chiefly with the *bacillus anthracis*, and the *staphylococcus pyogenes aureus*. As will be seen, the problem is one of disinfection, the toxic action of the various substances being investigated. The bacteria were distributed over the surfaces of carefully washed and completely disinfected garnets of equal size. That approximately the same number of bacteria should be used in each experiment, the same number of garnets was employed, and the mean of six results was taken. The garnets were placed in vessels made of platinum gauze, and introduced into the solution, which was kept at a constant temperature. After the action had taken place as long as desired, it was instantly brought to an end by adding some sub-

[1] Botan. Centralb., 76, 289, 321, 361, 391 (1898).
[2] Ztschr. phys. Chem., 21, 414.

stance which destroyed the disinfecting property of the solution. The spores were then washed from the garnets by shaking in water, and agar-agar jelly added to the water containing the spores. This mixture was poured into convenient dishes, and kept at a constant temperature. The bacteria, which were still alive, began to form distinctly visible colonies in twenty-four hours, and could easily be counted. The number of colonies was found to depend upon the time during which the toxic reagent acted, and upon the concentration of the solution. In general, the more dilute the solution the less the disinfecting action. The nature of the solvent was found to effect the relative toxic action of compounds.

Some of the more important results obtained by Paul and Krönig are: —

The disinfecting action of metallic salts depends, not only on the concentration of the metal in the solution, but also on the specific properties of the salt and the solvent.

The action of a salt of a metal depends not only on the specific action of the metallic ion, but also on that of the anion, and of the undissociated part of the salt.

Solutions of metallic salts, in which the metal forms part of a complex ion, are only weakly disinfecting.

The strong acids are toxic, not only in proportion to the concentration of the hydrogen ions, but the specific properties of the anions come into play. The bases which are equally dissociated, such as potassium, sodium, and lithium hydroxides, have the same disinfecting action. The weakly dissociated base, ammonium hydroxide, disinfects much less.

The disinfecting action of the halogens, Cl, Br, I, like

their chemical action, decreases with increasing atomic weight.

Solutions of substances in absolute alcohol and ether are almost without action on *bacillus anthracis*.

The disinfecting action of mercuric chloride and silver nitrate in alcohol is increased by the addition of more and more water.

These results are very interesting, as being an application of the theory of electrolytic dissociation in an entirely new direction. We have here a clear recognition of dissociation in the field of bacteriology.

**Toxic Action of Substances on Certain Fungi.**—We have seen the relation between the dissociation of solutions and their toxic action on certain phanerogams, as brought out by the work of Kahlenberg, True, and Heald; also the same relation when lower forms of life, the bacteria, were used. We must refer, in this connection, to the very recent investigation of Clark, in which the toxic action of substances on certain fungi was studied, and this action compared with the dissociation of the substance. Five fungi were used, and all were found to be much more resistant to injurious agents than the higher plants. The spores of moulds require, to inhibit germination, from two to four hundred times the strength of acid which is fatal to the higher plants. The hydroxyl ion was found to be more toxic to moulds than the hydrogen ion. The toxic value of the ions, $\bar{Cl}$, $\bar{Br}$, $\bar{I}$, increases with increasing atomic weight. It was found that in the case of several acids dissociation lessens their activity, the molecule being more active than the ions. Of the eight acids investigated, six were more active in the molecular than in the ionic form. The toxic

action of the molecule, in the case of hydrocyanic acid, was as much as 76.6 times that of the hydrogen ion. The anions of hydrochloric, nitric, and sulphuric acids are only slightly toxic to fungi.

These results, like those previously described, show that both molecules and ions may be poisonous to certain forms of life, just as both molecules and ions may be colored. The poisonous nature of the molecule or ion depends greatly upon the nature of the plant on which it acts.

**Application of the Dissociation Theory to Animal Physiology.** — The theory of electrolytic dissociation has been applied not only to vegetable, but has already found its way into animal physiology. The work of Loeb[1] was the first of importance in this field. He studied the action of certain electrolytes on the muscle of a frog. When the muscle from the leg of a frog is placed in a 0.7 per cent solution of sodium chloride, and a small amount of acid or base added to the solution, the muscle, by taking up water, undergoes an appreciable increase in weight. Loeb determined the increase in the weight of the muscle, produced by hydrochloric acid, nitric acid, and sulphuric acid, of known concentrations, and was led to this interesting conclusion. Solutions of these three acids, which contain the same number of hydrogen atoms in equal volumes, produce the same increase in the weight of the muscle. He showed that it is only the hydrogen cation which is active, the anion having little or no effect; and that when the same number of hydrogen ions is contained in equal volumes of their solutions, all of these acids produce exactly the same effect.

[1] Pflüger's Archiv f. Physiologie, 69, 1.

This does not hold for the weakly dissociated organic acids, since, in these cases, the anions as well as the molecules exert an influence. Loeb then studied the action of the following bases: lithium hydroxide, sodium hydroxide, potassium hydroxide, strontium hydroxide, and barium hydroxide, and found that they all had the same influence in causing the muscle to take up water, when they are used at such concentrations that an equal number of hydroxyl groups is contained in equal volumes of each of the solutions. The action of all these alkalies was found to depend entirely upon the anion of the base, *i.e.* hydroxyl; just as the action of the strong mineral acids depended entirely upon the cation hydrogen. The hydroxyl ions have, however, a stronger influence than an equal number of hydrogen ions. Solutions of potassium and sodium carbonate also cause the muscle to take up water. This is due to the hydroxyl ions in their solutions, formed by the hydrolysis of the salt and the subsequent dissociation of the base.

That the theory of osmotic pressure, deduced by van't Hoff, applies to this phenomenon, is shown by the fact that solutions of lithium, potassium, rhubidium, cæsium, magnesium, calcium, barium, and strontium chlorides, produce the same change in the weight of the muscle as a solution of sodium chloride of equal osmotic pressure.

Loeb also studied the toxic action of a number of ions on muscle, and found that for any given group, as $\overset{+}{Li}$, $\overset{+}{Na}$, $\overset{+}{K}$, $\overset{+}{Rb}$, $\overset{+}{Cs}$, the relative toxic action is proportional to the migration velocity of these ions, and not to their atomic

weights. The same relation obtains for the ions, $Be^{++}$, $Mg^{++}$, $Ca^{++}$, $Ba^{++}$, $Sr^{++}$, but does not extend from one natural group of the elements to another.

A second investigation was carried out by Loeb,[1] which is an extension of the one just considered. While the physiological action of the inorganic acids is conditioned by the number of hydrogen ions present, there is an apparent exception presented by the organic acids. The physiological activity of the fatty acids is not proportional to their dissociation. Thus, lactic acid, which, at the dilution employed is only eleven per cent dissociated, causes the muscle to take up as much water as trichloracetic acid and oxalic acid, in which nearly all of the molecules are dissociated. Similarly, mandelic acid causes the muscle to take up as much water as the more strongly dissociated organic acids, although, at the dilution used, it is only nineteen per cent dissociated. Loeb does not offer any final explanation of this phenomenon, but suggests that since the difference in the action of the different acids is so much less than the difference in their dissociation, it seems probable that those acids which are very slightly dissociated are transformed in the muscle into products with stronger dissociation. The author offers this as a possible explanation, and promises further investigation, especially with the aromatic acids.

**Physical Chemical Methods applied to Animal Physiology.** — Physical chemical methods have been applied by Bugarszky and Tangl[2] to a very different physiological problem. They have been employed to determine the con-

[1] Pflüger's Archiv f. Physiologie, 71, 457. [2] *Ibid.*, 72, 531.

centration of the dissolved substances in the blood serum, and also the relation between the electrolytes and non-electrolytes contained in it.

The freezing-point method was used to determine the molecular concentration of the dissolved substances. The freezing-point of the serum was first determined, then the freezing-point of pure water. Since blood serum is practically water containing electrolytes and non-electrolytes, the difference between the two freezing-points is the lowering of the freezing-point of water produced by the substances present in the blood serum. A gram-molecular solution of a non-electrolyte freezes 1.87° lower than pure water. To determine, therefore, the number of gram-molecular concentrations to which the substances in blood serum are equivalent, the difference between the freezing-point of water and of blood serum must be divided by 1.87. In this calculation the ions which result from the dissociation of any electrolytes present are treated as if they were molecules, since an ion produces the same lowering of the freezing-point as a molecule.

The above method shows the total concentration of electrolytes and non-electrolytes present in blood serum, but does not enable us to determine the amount of each. To accomplish this, some method must be employed which will enable us to discriminate between undissociated molecules and ions. Molecules in solution do not conduct the electric current; only ions conduct. We can, therefore, use the conductivity method to determine the amount of electrolytes present in the serum. This was done by Bugarszky and Tangl. The electrolytes present in blood serum are, almost all, salts. The alkaline reaction of the blood comes

from a few hydroxyl ions, which result from the hydrolysis of carbonates in the blood. Further, the salts in the blood are nearly all inorganic; organic salts being present only in very small quantity. The conductivity method is used as an approximate measure of the inorganic salts present, and is regarded as more accurate than the method of determining the amount of ash obtained from the serum. While the serum contains the cations, $\overset{+}{Na}$, $\overset{+}{K}$, $\overset{++}{Ca}$, $\overset{++}{Mg}$, and the anions $\overset{-}{Cl}$, $\overset{=}{CO_3}$, $H\overset{-}{CO_3}$, $H\overset{=}{PO_4}$, $\overset{=}{SO_4}$, $\overset{-}{OH}$; the main ions are $\overset{+}{Na}$, $\overset{-}{Cl}$, and some $\overset{=}{CO_3}$.

The determination of the concentration of the electrolytes in the blood serum, by the conductivity method, is somewhat complicated by the presence of the non-electrolytes in the serum, as the authors point out. The conductivity of an electrolyte is diminished by the presence of a non-electrolyte, and the magnitude of the effect depends both upon the nature of the electrolyte and the non-electrolyte. The non-electrolytes in the blood serum consist chiefly of albumens, with traces of a number of other substances. The albumens were isolated, and their effect on the conductivity determined. One gram of albumen in 100 cubic centimetres of blood serum, diminished the conductivity 2.5 per cent. By applying this correction to the observed conductivity of the serum, we obtain its true conductivity. The corrected conductivity can be used for calculating the concentration of the electrolytes dissolved in the serum. Knowing the amount of the electrolytes in the serum, it is a very simple matter to determine the amount of the non-electrolytes. The freezing-point method gives the sum of the two, as already stated. By subtracting from the

sum the amount of the electrolytes, we have at once the quantity of the non-electrolytes.

A number of conclusions of interest and importance were reached through this work, but since these lie almost wholly in the field of physiology, they do not come within the scope of this book. The authors point out that these same methods can, and should be applied to other liquids in the animal body.

**Application of Osmotic Pressure and Dissociation to the Mechanics of Secretion.** — The work of Dreser[1] illustrates the application of van't Hoff's laws of osmotic pressure and the theory of electrolytic dissociation, to the mechanics of secretion. The problem is to calculate the work done by the kidneys in secreting urine. This is accomplished by determining the osmotic pressure of the blood serum, and also that of the urine. There is no direct method of measuring osmotic pressure, which is of general applicability, so that an indirect method must be employed. The well-known freezing-point method was used, and from the difference in the freezing-point of the serum and of the urine, the difference in their osmotic pressures was calculated. If the volume secreted by the kidneys is taken into account, the osmotic work done by the kidneys is ascertained. And if we note the time during which the secretion takes place, the osmotic work done by the kidneys can be expressed in C.G.S. units.

A number of other investigations have already been carried out, in which the theory of electrolytic dissociation and the van't Hoff laws of osmotic pressure have been applied to biological problems. We should mention es-

[1] Archiv f. experimentelle Pathologie, **29**, 301.

pecially the work of Dreser,[1] Hamburger,[2] Hedin,[3] Heidenhain,[4] van Karányi,[5] and van Limbeck.[6] But the investigations already referred to, suffice to show the nature of the biological questions upon which modern physical chemistry is throwing light.

It would seem that the theory of electrolytic dissociation must find wide application in pharmacology. If chemical action is due mainly to ions, it is very probable that the pharmacological action of many chemical substances is largely ionic. This probability is increased, when we consider how many electrolytes are used in medicine, and that they are either taken in solution, or pass into solution in the fluids of the body. It is quite safe to predict, that many interesting and important results await the investigation of the relation between the dissociation of drugs, and their action upon the human body.

## CONCLUSION

By following a few of the many applications of the theory of electrolytic dissociation to problems in chemistry, physics, and biology, we can form some conception of its wide-reaching significance. The examples which have been taken up and studied are, in each case, a few chosen from the many. And if so much has been done in the short time which has elapsed since the theory was pro-

[1] Ztschr. phys. Chem., 21, 108.

[2] Du Bois' Archiv, 1886, 476; Virchow's Archiv, 140, 539; Centralb. f. Physiologie, 1893–94, 24.

[3] Skandinav. Archiv f. Physiologie, 5, 238, 385; Pflüger's Archiv f. Physiologie, 68, 248.

[4] Pflüger's Archiv, 56, 600.

[5] Centralb. f. Physiologie, 1893, Heft 3; Ungar. Archiv f. Med., 1895.

[6] Archiv f. exper. Pathologie, 25, 64.

posed, what may we not reasonably expect from the future? Since so many substances are broken down into ions, by water and similar solvents, it is almost certain that our theory will find application wherever aqueous solutions of electrolytes are employed. A moment's reflection will show that comparatively few branches of natural science lie wholly without its scope.

A careful study of the applications of the theory, which have already been made, will bring out a fact of profound significance. The theory cöordinates and correlates heterogeneous masses of facts, which apparently bore little or no relation to one another, and refers them to a common cause. As an illustration, take the neutralization of acids and bases, or the strength of acids and bases in general. But this is just what the physical chemistry of to-day has done, and is doing for several branches of science, and especially for the science of chemistry. Physical chemistry is furnishing us, largely with the aid of the theory of electrolytic dissociation, with rational explanations of chemical processes whose meaning was entirely concealed, and is rapidly placing chemistry upon that exact mathematical basis which physics has so long enjoyed.

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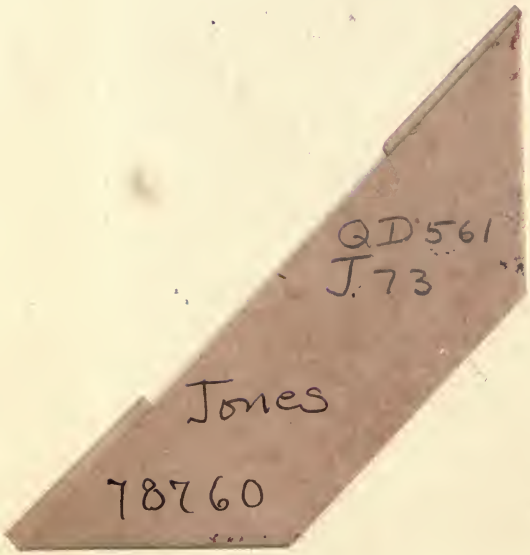
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